High refractive index immersion liquid for super-resolution 3D imaging using
sapphire-based aNAIL optics

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Optically-transparent immersion liquids with refractive index (n ~ 1.77) to match sapphire-based aplanatic numerical aperture increasing lens (aNAIL) are necessary for achieving deep 3D imaging with high spatial resolution. We report that antimony tribromide (SbBr₃) salt dissolved in liquid diiodomethane (CH₂I₂) provides a new high refractive index immersion liquid for optics applications. The refractive index is tunable from n = 1.74 (pure) to n = 1.873 (saturated), by adjusting either salt concentration or temperature; this allows it to match (or even exceed) the refractive index of sapphire. Importantly, the solution gives excellent light transmittance in the ultraviolet to near-infrared range, an improvement over commercially-available immersion liquids. This refractive index matched immersion liquid formulation has enabled us to develop a sapphire-based aNAIL objective that has both high numerical aperture (NA = 1.17) and long working distance (WD = 12 mm). This opens up new possibilities for deep 3D imaging with high spatial resolution.

I. INTRODUCTION

Sapphire-based aplanatic numerical aperture increasing lenses (aNAIL) [1, 2] provide a promising route to achieve super-resolution 3D imaging [3], but their development requires a suitable refractive index-matching liquid (n ~ 1.77). A typical aNAIL design would include a truncated aplanatic solid immersion lens of plano-convex shape, made of high refractive index solid material [4–6] such as sapphire [7, 8]. To date, the lack of a suitable immersion liquid has limited the application of aNAIL to subsurface microscopy of objects immersed inside a refractive index-matched solid medium, without the possibility of depth-scanning [1, 2, 6]. Therefore, a refractive index-matched immersion liquid will allow for simultaneously harnessing both the high spatial resolution and the depth scanning capability of sapphire-based aNAILs [3]. However, a persistent challenge in the search for high refractive index immersion liquids is to find one with both low absorbance and low scattering. The ideal liquid would provide optical transparency across the full spectrum from ultraviolet to near-infrared, as well as tunability to provide precise index-matching [9].

A promising candidate solvent is the organic liquid diiodomethane (CH₂I₂), which is one of the liquids with highest known refractive index values (n = 1.74). While other high refractive index liquids exist (phenyldi-iodoarsine (C₆H₅AsI₂) with n = 1.85 and selenium monobromide (Se₂Br₂) with n = 2.1 [10]), diiodomethane has the key advantage of being commercially available. In addition, diiodomethane is an excellent solvent, and many liquid formulations using salts dissolved in diiodomethane are reported to increase the refractive index [10] and are even available commercially (Cargille labs, Series M, n = 1.8). However, the strong light scattering and high absorbance of these formulations render them insufficiently transparent for high-resolution optics applications. A lack of knowledge of a salt formulation to increase the refractive index while maintaining optical transparency has caused diiodomethane to remain under-utilized as a preferred immersion solvent liquid, despite its inertness with many minerals (including sapphire) [10].

The refractive index of an optical medium is typically proportional to its mass density, as described by the Lorentz-Lorentz equation [11]; this suggests that salts containing heavy elements would be promising candidates. In addition, a large electronegativity difference between the salt cation and anion typically predicts improved solubility. Guided by these principles, we screened four different salts – antimony tribromide (SbBr₃) [10], antimony trichloride (SbCl₃), barium chloride (BaCl₂), and bismuth trichloride (BiCl₃) – as potential solutes in CH₂I₂. Of this list, BaCl₂ and BiCl₃ were found to have poor solubility due to small cation-anion electronegativity differences. Despite the excellent solubility of SbCl₃, the refractive index increased only by 0.02, due to the low atomic weight of chlorine. Therefore, only SbBr₃ was found to be a suitable candidate: for concentrations between 20 wt% and saturation in liquid CH₂I₂, it achieves a refractive index as high as n ~ 1.873. In addition, this solution shows excellent optical transparency and low scattering in the wavelength ranges λ < 350 nm and 450 nm < λ < 1060 nm. Below,
we present measurements quantifying the concentration, temperature, and wavelength dependence of the index of refraction, transmittance, and scattering of these liquid solutions.

II. METHODS

We prepare liquid solutions of different concentrations (wt%) from a powder sample of SbBr$_3$ (99% pure, Alfa Aesar) dissolved in the liquid CH$_2$H$_2$ (99% pure, Sigma-Aldrich). To obtain a solution of given wt%, we mix the two components in the desired weight ratio, first on an electrical shaker for six hours at $T = 22$ °C and then in a centrifuge for 3 hrs at 800 rpm at $T = 15$ °C. We then separate the upper (supernatant) liquid solution from the precipitate (assumed to contain chemical impurities) collected at the bottom of the centrifuge tube. For a 50 wt% concentration at room temperature ($T = 22$ °C), crystals are also formed that remain in equilibrium with the supernatant (saturated) solution. Note that the chemical handling of both components requires significant care. Antimony tribromide is harmful if swallowed (H302) or inhaled (H332), and is is hygroscopic (absorbs water). Diiodomethane is harmful if swallowed (H302), causes skin irritation (H315), and serious eye damage (H318), and also may cause respiratory irritation (H335).

We perform index of refraction measurements using a liquid refractometer based on the design of Nemoto [12], as shown schematically in Fig. 1. The apparatus determines the displacement $\delta$ of a laser beam, due to passing through a liquid-filled cuvette rotated by an angle $\theta$ with respect to the beam. The center of the laser beam is determined by scanning a knife edge across its profile. As shown in the inset of Fig. 2, the light intensity profile $P(x)$ is well-described by an error function, as expected for a single-mode laser. We identify the center of the beam as the location $x$ at which $P(x)$ rises fastest, as obtained by numerical differentiation. Sample Gaussian beam profiles $dP/dx$ are shown in Fig. 2 characterized by the beam width $w$ at which the power falls by a factor of $1/e^2$ [13, 14]. Throughout the measurements, we control the temperature of the liquid to ±0.05°C by encapsulating the quartz cuvette (Hellma Analytics) inside a rectangular copper block containing channels connected to a refrigerated water bath circulator (Neslab RTE 111). The copper block is mounted on a rotation stage with a vernier scale which provides an angular reproducibility of ±5 arcmin.

Following Nemoto [12], the refractive index $n$ of the liquid can be calculated from

$$n = n_0 \sin \theta \sqrt{1 + \left(\frac{\cos \theta}{\sin \theta - \Delta/d}\right)^2}$$

(1)

where $n_0$ is the refractive index of air (the empty cuvette), $d$ is the width of the cuvette, and $\Delta \equiv \delta - \delta_0$ is the relative displacement of the Gaussian peak for the liquid-filled cuvette relative to the empty cuvette.

To obtain $n$, we repeat the same measurement at 7 different incident angles $\theta = (\pm10^\circ, \pm20^\circ, \pm30^\circ, \pm40^\circ)$, corresponding to both clockwise and counter-clockwise rotation of the cuvette with respect to the incident light. The average of these 7 measurements provides the value of $n$ for each combination of wavelength, temperature, and SbBr$_3$ concentration. We repeat this process for 3 wavelengths of light ($\lambda = 473, 532$, and 633 nm), 5 temperatures from 15°C to 40°C, and 3 concentrations (20 wt%, 33.5 wt%, and saturation concentration).

Eq. 1 already reduces systematic errors due to geometric imperfections of the cuvette by measuring all values of $\delta$ against the empty cuvette. In addition, we have analyzed the systematic errors in our setup and determined...
that the precision of the rotation stage and the imperfect parallelism of the cuvette sidewalls are the largest sources of error. These combined effects result in a refractive index measurement error of ±0.003. In practice, we find that we are able to measure the refractive index of water and ethanol to within ±0.001 of values reported in the literature [15–17].

III. RESULTS

A. Index of Refraction

We find that SbBr₃ dissolved in CH₂I₂ can meet and exceed the index of refraction of sapphire over a broad range of temperatures, visible wavelengths, and concentration greater than 20 wt%. Fig. 3 presents the measured values of n as a function of wavelength (panels a-c), temperature (plot absissa), and concentration (line series). In each case, the refractive index can be increased by either changing the concentration (more dissolved salt corresponds to higher n) or the temperature (higher temperature decreases n). In applications, preparing a solution of known concentration is more convenient for coarse tuning, and temperature is more convenient for fine tuning in-situ. The largest value we measure is n = 1.873, for saturated solutions at low temperature and short wavelength.

B. Optical Transparency

Optical transparency, which can be degraded by both light scattering and absorption, plays a crucial role in determining the utility of an immersion liquid. We characterize these properties of the SbBr₃-CH₂I₂ solutions, and compare with the two commonly-used commercial high refractive index immersion liquids (Cargille M Series with n = 1.71 ± 0.0005 and n = 1.80 ± 0.0005). Fig. 4 shows the transmittance spectra, measured from the near-ultraviolet to the near-infrared. The illumination source is an Ocean Optics tungsten-halogen light source (model HL-2000-FHSA-LL with output power 4.5 mW) and transmitted light is recorded on an Ocean Optics spectrometer (model HR2000+). For all five liquid solutions, there is a significant absorption band centered around 410 nm (blue). In addition, there are several coincident absorption bands located at λ = 725, 887, and 1037 nm, which possibly arise due to the common solvent CH₂I₂ used for all five liquids.

Furthermore, we observe a Tyndall effect at all the three wavelengths, with stronger scattering for the Cargille liquids than for our SbBr₃ solutions. This suggests that Mie scattering is present, caused by colloidal particles with a size on the same order as λ [18]. In order to quantify the amount of scattering, we measure the relative increase in beam width ∆w = (w - w₀) / w₀, where w and w₀ are the beam-widths for the liquid and air-filled cuvettes, respectively. A large value of ∆w signifies stronger scattering. For simplicity, all measurements are done at T = 25°C and for normal incidence (θ = 0°), using the knife-edge scanning method shown in Fig. 2. Results for the two wavelengths 473 and 633 nm are given in Table I.

At λ = 633 nm, the beam width remains unaffected for the SbBr₃-CH₂I₂ liquid solutions and the Cargille liquid n = 1.71. Only the Cargille n = 1.80 liquid contains colloidal particles in the relevant size range. At λ = 473 nm, the beam width also shows a concentration-dependent increase for the SbBr₃-CH₂I₂ liquid solutions. A likely source of particles in this diameter range is that hydrolysis with atmospheric humidity produces small antimony oxide crystals via the reaction 2SbBr₃ + 3H₂O → Sb₂O₃ + 6HBr [19]. At the same wavelength, the Cargille liquid n = 1.71 shows an even stronger scattering, while the opacity of the n = 1.8 Cargille liquid does not even allow the measurement of the beam width.

C. Physical Properties

We characterize the volumetric thermal expansion coefficient (γ) and the density (ρ) of the liquid solution (SbBr₃+CH₂I₂) as a function of concentration, using a dilatometer (PHYWE Systeme GmbH) and pycnometer (BRAND GmbH), respectively. We observe that decreasing the concentration of SbBr₃ from the saturated case increases γ by 50% and decreases ρ by 4%, as shown in Table IV. Because SbBr₃ reacts with H₂O, the liquid solution (SbBr₃+CH₂I₂) is immiscible in water (see Sec 3.B for details).

IV. DISCUSSION

Antimony tribromide (SbBr₃) dissolved in diiodomethane (CH₂I₂) is a strong candidate as an immersion liquid for sapphire-based aNAIL lenses (see Fig. 5a). Together with a refractive index matched immersion liquid, these lenses allow for the simultaneous increase of both the numerical aperture (NA, the light-gathering power) and the working distance (WD) of an

| Liquid/liquid solution | Beam width increase(%) |
|------------------------|-------------------------|
| Diiodomethane (CH₂I₂)  | 0 / 2.2                 |
| 20 wt% SbBr₃ solution  | 0 / 9.5                 |
| 33.5 wt% SbBr₃ solution| 0 / 10.6                |
| Cargille liquid (n=1.71)| 1.2 / 16                |
| Cargille liquid (n=1.80)| 13.5 / Opaque           |

TABLE I: Proportional increase (%) in the beam width, referenced against an empty cuvette.
TABLE II: Physical properties of the liquid solutions of different concentrations. All density measurements were performed at \( T = 22 \, ^\circ\text{C} \). The temperature ranges, over which the volumetric thermal expansion measurements were performed, were \( T = 23 - 35 \, ^\circ\text{C} \), \( 20 - 32 \, ^\circ\text{C} \) and \( 25 - 36 \, ^\circ\text{C} \) for 20 wt\%, 33.5 wt\% and saturated solution, respectively.

| Liquid solution          | Thermal expansion coefficient, \( \gamma \) (K\(^{-1}\)) | Density, \( \rho \) (gm/mL) |
|--------------------------|------------------------------------------------------------|------------------------------|
| 20 wt\% SbBr\(_3\) solution | 6.9 \times 10^{-4}                                          | 3.422                        |
| 33.5 wt\% SbBr\(_3\) solution | 5.4 \times 10^{-4}                                          | 3.504                        |
| Saturated SbBr\(_3\) solution       | 4.6 \times 10^{-4}                                          | 3.572                        |
high-$n$ liquid has limited the range of tunable optical power, as this depends on the difference of the refractive indices of the two immiscible liquids used to build the adaptive liquid lens [21–23].

Finally, we close with the application that inspired our work on this immersion liquid formulation: the imaging of gems made from corundum minerals (ruby and sapphire), which have $n \sim 1.77$. High spatial resolution lenses such as those described above (aNAIL) would open new routes to studying the crystallization process during mineral formation [24] and quality in manufacturing industry (gemstone, watch etc.) [25]. Importantly, ruby also has a pressure-dependent fluorescence peak [26–28], which has recently been exploited as a tool for measuring the pressure field inside rubies themselves [29, 30].

V. CONCLUSION

We have demonstrated that antimony tribromide ($\text{SbBr}_3$) dissolved in diiodomethane (CH$_2$I$_2$), for concentrations between 20 wt% and saturation, provides a promising new high refractive index liquid formulation. At standard conditions for temperature and pressure (STP) and at wavelengths from near-ultraviolet to near-infrared, we observe that $n > 1.77$ (sapphire) is attainable. For optimized choice of parameters (low temperature, short wavelength, high concentration), we can achieve $n = 1.873$. In addition, this liquid is observed to have high transmission and low scattering for $\lambda < 350$ nm and $\lambda \gtrsim 450$ nm. On using this liquid formulation as refractive index matched immersion medium, we have developed a sapphire-based aplanatic numerical aperture increasing lens (aNAIL) that has both high numerical aperture $NA = 1.17$ and long working distance (WD = 12 mm). This paves the way for deep 3D imaging with high spatial resolution. Moreover, the tunability of this extremely high $n$ liquid has several other promising applications, particularly in the development of adaptive liquid lens, gemstone, watch industry etc.

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