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Optimizing the transparency of nano-LiF:Cu/silicone nanocomposites for 3D optically stimulated luminescence dosimetry

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Abstract. Nanoparticles displaying optically stimulated luminescence embedded in a transparent polymer matrix have been proposed as a reusable high-spatial resolution 3D dosimeter. We measured the refractive indices of LiF:Cu nanoparticles and silicone and found a mismatch of 0.03-0.05 for the relevant wavelengths, explaining the transmission loss through 1 cm-sized nanocomposite dosimeters. We propose to bridge the refractive index gap by coating the LiF nanoparticles with a shell of SiO_2. Initial studies show successful SiO_2 growth, although more work is required to produce core-shell nanoparticles with an optimized refractive index.

1. Introduction

Recently, there has been significant progress in the development of a reusable, high-fidelity 3D dosimeter based on optically stimulated luminescence (OSL) [1–3]. OSL is a well-known technique for integrating dosimetry based on charge carriers excited by ionizing radiation becoming trapped in metastable dosimetric trap states within the band gap of an insulator. To read out the trapped charge – which is ideally proportional to the deposited dose – a light source is used to promote the carriers to the conduction (or valence) band. Once mobile, the charges can recombine radiatively giving the designated OSL signal. To reduce cost and at the same time enable large dosimetric volumes, a composite dosimeter consisting of OSL active nanoparticles embedded in an elastomer matrix has been proposed. Copper-doped LiF nanocubes (nLiF:Cu) of ∼50 nm side length were recently identified as a viable candidate material for the nanoparticles [3]. The particles show a high OSL signal emitted in the UV region, which can be stimulated with visible light such as green and blue lasers. Furthermore, they seem close to ideal for embedment in silicone (polydimethylsiloxane) thanks to the near match of their refractive indices. This is also illustrated by the high transparency of mm-thick 2D sheets of nLiF in silicone [3].

An important next step in scaling up the nanocomposite dosimeters from 2D to 3D is optimizing the transparency to secure the necessary transmission of light through large volumes. Light scattering can be minimized for example by lowering the particle size below the wavelength of the light to reduce Mie scattering and by matching the refractive indices perfectly. This can be done by adjusting the refractive index of either the matrix or the nanoparticles. The latter can for instance be done by employing the observation that the effective refractive index of a core-shell particle to a good approximation (for small particles and relatively thin coatings) will be the volume-average of the pure substances [4].

In this contribution, we will report the refractive index mismatch between nLiF:Cu and a silicone matrix and present preliminary investigations of using a SiO_2 shell on the LiF nanoparticles to adjust their refractive index.

2. Materials and methods

Copper-doped LiF nanoparticles were prepared by mixing precursors carrying the different constituents in a home-built flow setup, as described in detail in [3]. The refractive index of nLiF:Cu was measured by dispersing a known amount of nanoparticles in solutions of known refractive index and measuring the transparency of these suspensions at the relevant wavelengths. This mimics the embedded state, and the value found for the refractive index of nanoparticles in this way is assumed similar to that exhibited by nLiF:Cu in a silicone nanocomposite. All transmission measurements were performed on a Perkin Elmer Lambda 1050 spectrophotometer in total transmission mode using an integrating sphere.

The nanocomposite samples were made by embedding a certain amount of nLiF:Cu particles in Dow Corning Sylgard 184 using a base to curing agent ratio of 10:1 and room temperature curing. The refractive index of pure silicone was measured using an LLG Labware uniREFRACTO 2 refractometer as it cured under the same conditions applied to the dosimeters.

SiO_2 shells were grown on the LiF:Cu nanoparticles using the modified Stöber process [5]. Using NH_3 in water to catalyze the hydrolyzation of tetraethyl orthosilicate (TEOS) to SiO_2, two samples were prepared with nominal shell thicknesses of 5 and 20 nm. The resulting nanoparticles were characterized by powder x-ray diffraction (PXRD, Rigaku Smartlab) and a combined scanning electron microscopy (SEM, FEI Nova NanoSEM) and energy dispersive x-ray spectroscopy (EDS, Ametek EDAX) study. Furthermore, the OSL and radioluminescence yield were found for uncoated and coated nanoparticles with a $^{90}Sr/^{90}Y$ β-ray source and a blue laser [3].

3. Results & Discussion

The wavelength dependent transmission of various concentrations of nLiF:Cu in silicone shown in Fig. 1a is consistent with the $1/\lambda^4$ relation expected for Rayleigh scattering [6]. There is a clear indication that the refractive indices are not matched perfectly, since the dropoff in transmission towards lower wavelengths is exacerbated by higher load levels of nanopowder in silicone. Since the OSL signal from the nanoparticles is at a wavelength of ~325 nm, where the transparency is already poor even at low concentrations of LiF, Fig. 1a clearly illustrates the inadequacy of the as-synthesized nanoparticles together with the standard silicone as a high signal-to-noise-ratio macroscopic 3D dosimeter.

Fig. 1b shows total transmission curves for various solutions with dispersed nanoparticles denoted by their refractive index at the wavelength of OSL emission. From these curves, the refractive index of the nanoparticles can be extracted. The observation that different solutions peak in transparency at different wavelengths (Fig. 1b) reflects the difference in dispersion between the nanoparticles and the solutions. The large band gap of nLiF:Cu results in an almost flat dispersion across a large wavelength range, whereas the organic solvents (methanol and ethylene glycol) used to prepare the reference solutions have a much more marked dispersion towards short wavelengths, in fact close to that of silicone. By using the maximum of each of these curves as an estimate for the wavelength at which the refractive index matches between the organic solvent and the nanoparticles, the colored points seen in Fig. 1c can be plotted. A fit to a first-order Sellmeier equation yields the solid black line. Also drawn is the tabulated dispersion curve of bulk LiF [7] (dotted black), which slightly exceeds that of nLiF. Note the identical color map between 1b and 1c, identifying the dispersion curves in Fig. 1c with the refractive index of each solution in Fig. 1b.

The refractive index of Sylgard 184 depends on the ratio of curing agent to base polymer and the curing temperature [8]. The measurement of the silicone used in the current work yielded a refractive index rising slightly with curing time before stabilizing at 1.4126(1) after 4 days (measured at 589 nm). Assuming a dispersion similar to the one measured in [9], the refractive index of silicone can be plotted

(Fig. 1c). The measurement in [9] was done on a temperature-cured sample of Sylgard 184 (at 150°C) the dispersion of which is not necessarily identical to that of a room-temperature cured sample. It can, nevertheless, provide a guide to the mismatch as a function of wavelength. The refractive index mismatch of 0.029 at a stimulation wavelength of 445 nm and 0.049 at an OSL emission wavelength of 325 nm indicates a potentially more serious problem than first anticipated from the transmission curves in Fig. 1a. These curves were measured using total transmission, thus also taking into account forward diffuse scattering, which is not included in the Rayleigh theory. Direct transmission measurements are therefore necessary to accurately determine the extent of the problem.

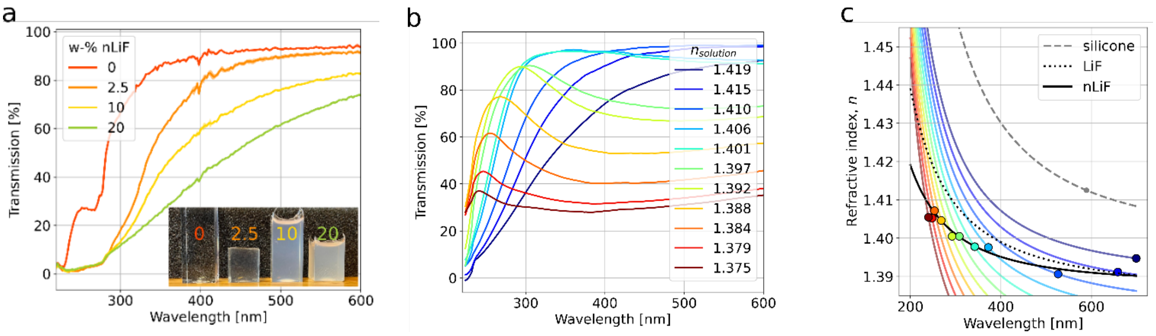

Figure 1. (a) Total transmission curves for four different cuvette-sized silicone molds with various weight fractions of nano-LiF powder. (b) Total transmission of 10 w-% nLiF:Cu powder dispersed in solutions of various refractive indices (n_{solution}) and (c) the refractive index of the nanoparticles as function of wavelength found by assuming a perfect match between the nanoparticles and the solution at the peak of the transmission curves in (b). The colored curves are dispersion curves of the solutions (see legend in (b)) obtained by interpolation between those of the pure solvents (methanol and ethylene glycol) measured in [10]. The refractive index of silicone shown in gray is based on the measurement at 589 nm extended to other wavelengths using tabulated values for the dispersion curve [9]. Also shown is the refractive index of nLiF (fit in solid black) and bulk LiF (from [7] in dotted black).

The mismatch between the refractive indices of the nanocrystals and silicone found above poses as a challenge for achieving the required transparency in a 3D OSL dosimeter. As a way of compromising for the too-low refractive index of the nanoparticles, a shell consisting of a material with a larger refractive index can be grown. SiO_2 has a moderately higher refractive index $n_{\text{SiO}_2} \sim 1.47$ at 400 nm, which motivates an attempt to grow LiF/SiO_2 core-shell nanoparticles.

The PXRD of the two different variations of core-shell nLiF:Cu/SiO_2 nanoparticles with nominal shell radii of 5 and 20 nm as well as the uncoated nLiF particles confirm the existence of LiF nanoparticles of ~50 nm both before and after the shell growth (see Fig. 2a). The coated samples in addition show a broad peak at $2\theta \approx 23°$ corresponding to amorphous nano-SiO_2 [11], which is rising with increasing SiO_2 content. The combined SEM and EDS study confirmed the presence of both F, Si, and O in the coated samples (note that Li cannot be detected by EDS), suggesting a successful synthesis. In fact, the Si/F ratios agree relatively well with the expected values assuming all TEOS to be hydrolyzed. The measured ratios give expected 3 and 27 nm shells as opposed to the nominal 5 and 20 nm. The SEM images of all samples reveal cubic nanoparticles with a very monodisperse size distribution around 51 nm with a standard deviation of 6 nm (see Fig. 2b for the 5 nm coated sample). This is seemingly at variance with the desired core-shell geometry. The morphology might be elucidated by EDS mapping using scanning transmission electron microscopy. This will be the focus of future study. The methodology for measuring the refractive index of nLiF presented in this contribution can be used on the coated samples as well, giving a straightforward way of identifying the optimal core-shell particles.

The effective dilution of the nLiF:Cu particles is reflected in scaled down intensities of both radioluminescence and OSL for the coated particles as compared to uncoated, while the emission wavelength and decay time remain the same. The observation that SiO_2 on and around the LiF:Cu nanoparticles does not seem to extinguish the OSL signal is encouraging for future applications of the Stöber process in modifying the refractive index.

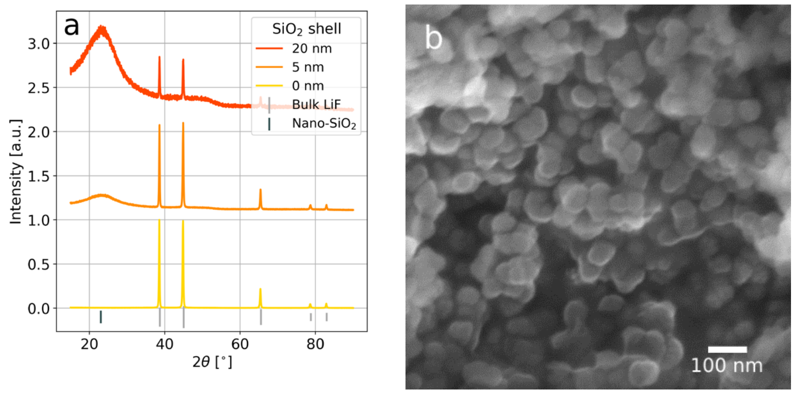

Figure 2. (a) PXRD data of uncoated and coated (with shells of nominally 5 and 20 nm SiO_2) nLiF:Cu. Expected peak positions for bulk LiF and nanosized amorphous SiO_2 are shown as bars on the bottom. (b) SEM image of the 5 nm SiO_2 coated nLiF:Cu sample. A large number of ~50 nm nanocubes can be seen.

A conceptually different strategy involves fully utilizing the nanosized nature of the particles. If the OSL properties can be conserved while lowering the particle size, the nanoparticles will practically disappear optically according to Rayleigh scattering theory. This would also mitigate the need to obtain transparency at two wavelengths (the stimulating and the emitted OSL light), which is challenged by the difference in dispersion between the two materials. Possibilities in controlling the particle size, for example by varying the precursors and/or solvents of the synthesis, will be the focus of future investigations.

4. Conclusion

The transparency loss caused by the mismatch in refractive index between the nanoparticles and the silicone matrix must be resolved before cm-sized dosimeters can be realized. Even though the as-synthesized LiF nanocubes have a refractive index relatively close to silicone, transmission measurements of nanocomposite dosimeters show a considerable scattering of light – especially at low wavelengths. An initial pilot synthesis showed formation of SiO_2, however not necessarily as a shell around the LiF nanocubes. The search for a successful synthesis yielding the optimal coating thickness is still ongoing.

5. References

[1] Nyemann J S *et al* 2022 *J. Phys. Conf. Ser.* (In press)
[2] Jensen M L *et al* 2022 *Sci. Rep.* **12** 8301
[3] Nielsen C L *et al* 2022 *Nano Lett.* **22** 1566-1572
[4] Kuzma A *et al* 2012 *J. Appl. Phys.* **112**
[5] Yang X *et al* 2013 *J. Mater. Chem. C.* **1** 3359-3366
[6] Jin Y et al 2016 *J. Mater. Chem. C.* **4** 3654-3660
[7] Li H H 1976 *J. Phys. Chem. Ref. Data.* **5** 329-529
[8] Santiago-Alvarado A *et al* 2020 *Mater. Res. Express.* **7** 45301
[9] Schneider F *et al* 2009 *Sensors Actuators, A Phys.* **151** 95-99
[10] Kozma I Z *et al* 2005 *J. Opt. Soc. Am. B.* **22** 1479-1485
[11] Sun J *et al* 2017 *Nanomaterials* **7** 1-15