Conley, Kevin; Moosakhani, Shima; Thakore, Vaibhav; Ge, Yanling; Lehtonen, Joonas; Karttunen, Mikko; Hannula, Simo Pekka; Ala-Nissila, Tapio

Silica-silicon composites for near-infrared reflection

Published in:
Ceramics International

DOI:
10.1016/j.ceramint.2021.02.257

Published: 15/06/2021

Document Version
Publisher's PDF, also known as Version of record

Published under the following license:
CC BY

Please cite the original version:
Conley, K., Moosakhani, S., Thakore, V., Ge, Y., Lehtonen, J., Karttunen, M., Hannula, S. P., & Ala-Nissila, T. (2021). Silica-silicon composites for near-infrared reflection: A comprehensive computational and experimental study. Ceramics International, 47(12), 16833-16840. https://doi.org/10.1016/j.ceramint.2021.02.257

This material is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.
Silica-silicon composites for near-infrared reflection: A comprehensive computational and experimental study

Kevin Conley a, Shima Moosakhani b, Vaibhav Thakore c,d, Yanling Ge b, Joonas Lehtonen b, Mikko Karttunen e,f,g, Simo-Pekka Hannula b, Tapio Ala-Nissila a,b,*

Keywords: sintering; composites; optical properties; SiO2

Abstract
Compact layers containing embedded semiconductor particles consolidated using pulsed electric current sintering exhibit intense, broadband near-infrared reflectance. The composites consolidated from nano- or micro-sized silica powder have a different porous microstructure which causes scattering at the air-matrix interface and results in a higher reflectance primarily in the visible region. The 3 mm thick composite compacts reflect up to 72% of the incident radiation in the near-infrared region with a semiconductor microinclusion volume fraction of 1% which closely matches predictions from multiscale Monte Carlo modeling and Kubelka-Munk theory. Further, the calculated spectra predict a reddish brown compact with improved reflectance can be obtained by decreasing the average particle size or broadening the standard deviation. The high reflectance is achieved with minimal dissipative losses and facile manufacturing, and the composites described herein are well-suited to control the radiative transfer of heat in devices at high temperature and under harsh conditions.

1. Introduction

Controlled propagation of near-infrared (NIR) electromagnetic waves has been demonstrated in diverse applications, including biosensing [1], thermal energy management [2], and switchable meta-mirrors [3]. The NIR region is the principal component of thermal radiation and accounts for 52% of the sun’s irradiance power [4]. Developing compact layers to trap light in the NIR could be used to provide quantitative spectral information about heat transport under harsh conditions [5] or increase efficiency and reduce cost in solar cells and thermal energy management [6–8].

Materials or devices employed in thermal insulation and Gradient Heat Flux sensing applications are subjected to high temperature and harsh conditions. Metallic particles are typically used in many applications because of their strong plasmonic response, but they suffer from intrinsic Ohmic losses [9]. In contrast, semiconductors have lower dissipative losses and the quality of the scattering resonances is better maintained than in metallic particles at high temperatures [10].

Composite compacts embedded with low volume fraction of low bandgap semiconductor microparticles, such as silicon or germanium, are predicted to reflect over 80% of NIR solar radiation [36] and up to 65% of blackbody radiation [12]. The strong reflectance is achieved with much lower volume fraction (1%) than compacts of similar thickness containing hBN-platelets at 50% volume fraction [13]. The light interacts with the particles to generate strong scattering resonances. Unique optical effects such as unidirectional scattering and enhanced Raman scattering arise when there is interference between the resonances and strong localization of the electric and magnetic fields [14–16].

Consolidating microparticles into a matrix (host) can be achieved by various techniques such as sol–gel [17], vapor phase axial deposition [18], pressureless sintering of floc-casting [19], slip-casting [20], and electric current assisted sintering (Pulsed electric current sintering, PECS or spark plasma sintering, SPS) [21]. Among these wide-ranging methods...
techniques, the rapid processing time of PECS is very effective at limiting diffusive transformations such as crystallization, oxidation, and grain growth even at elevated processing temperatures. On the other hand, this technique provides a facile route to achieve the required thickness in comparison with other methods like sol-gel that would need successive layer-by-layer deposition. Typical heating rates in PECS range from 5 °C/min up to 2000 °C/min, and the typical sintering times are in minutes [21]. PECS has been used in the consolidation of SiO₂ composite layers. Singh et al. synthesized a silica/graphene oxide (GO) composite with a GO content ranging from 0.001 to 10% [22]. The silica/GO compacts were consolidated at a temperature of 1200 °C at a heating rate of 100 °C/min with a hold time of 1 min at a pressure of 50 MPa. He et al. made a SiO₂/SiC composite using SiC deposited by use of PVD onto SiO₂ particles [23]. They observed that the densification during the PECS began at 1127 °C of SiO₂ with the highest density obtained at 1277 °C and above, but the NIR reflectivity of the compact layers prepared by PECS was not examined.

In this study, highly dense SiO₂ compacts embedded with silicon particles are synthesized by PECS and their diffuse reflectance spectra are compared with results from Monte Carlo simulations and Kubelka-Munk theory from the mid-ultraviolet to NIR. The synthesis, characterization, and computational methodologies are described in Section 2. The porosity and microstructure of the experimentally prepared silica-silicon particle composites are described in Section 3.1. In Section 3.2, the optical properties of silica-silicon composite compacts of various thickness are calculated and compared with experiments. The optical properties of composites containing various particle size distributions are presented in Section 3.3. The conclusions and implications for applications are outlined in Section 4.

2. Materials and methods

2.1. Materials

Crushed silicon was purchased from Alfa Aesar. SEM imaging of the Si powder indicates that the received particles have an irregular shape (Figure A1). Two fused silica powders, nano- and micron-sized silica powders, with a nominal particle size of 8 nm (from Sigma Aldrich) and 1 μm (from Alfa Aesar) correspondingly were employed.

2.2. Composite compact preparation

Reference silica and composite silica-silicon compacts were prepared by pulsed electric current sintering. Silicon particles were mixed with fused silica using Willy Bachofen Turbula Mixer for 2 h. The reference silica powder or the mixed composite powder was placed into a mold with a 20 mm diameter. A 0.2 mm graphite foil was wrapped around the mold to ensure a tight fit. A heating rate of 100 °C/min and pressure of 50 MPa were applied during the entire experiment. A degassing step was used during the heating at 600 °C for 3 min to allow any gases in the powder to escape. All samples were sintered at a temperature of 1200 °C for 3 min for micro SiO₂ and 1 min for nano SiO₂. The graphite paper was removed from the samples, and the samples were ground to a final surface quality using 1200-grit SiC paper followed by mechanical polishing using diamond paste with 6 μm, 3 μm, and 1 μm particle sizes. The prepared samples were 20 mm in diameter and 3 mm in thickness. The density of the samples was measured by the Archimedes method using deionized water.

2.3. Characterisation

The microstructure of the samples was measured using X-ray diffraction (XRD) with a PANanalytical Xpert Pro powder with a Cu anode (K α) X-ray source. Field emission scanning electron microscopy (FESEM) images were obtained by TESCAN Mira 3 and Focused Ion Beam (FIB) Jeol JIB 4700 utilizing a field emission cathode. The UV–Vis–NIR diffuse reflectance spectrum was recorded in the wavelength range 250–2500 nm using a UV–Vis–NIR Agilent Cary 5000 equipped with diffuse reflectance accessories (integrating sphere). Static Light Scattering measurements were obtained with a Mastersizer 2000.

2.4. Radiative transport simulations

The optical properties of the silica compacts embedded with silicon were calculated using a modified Monte Carlo method [12] adapted from Wang et al. [24]. A spherical particle with radius, r, was surrounded by a non-absorbing insulating medium with constant refractive index of 1.5 and irradiated by light, λ = 250–2500 nm. The dielectric function of silicon was obtained from Palik [25]. The efficiencies of scattering, Qscat absorption, Qabs, and scattering asymmetry factor, g, of a single particle in an incident electromagnetic field were calculated using the full solutions of Lorenz-Mie theory and are described in the Supplementary Material.

Here, the microparticles were well-distributed in a non-absorbing insulating matrix with a volume fraction, f, up to 1%. The compact thickness, t, was varied from 50 μm to 3 mm, and was surrounded by a non-absorbing ambient medium. The results from theory were performed using the particle size distribution, P(r), obtained from Static Light Scattering measurements. The ensemble averaged scattering and absorption coefficients, μsca and μabs, of the compact are

$$\mu_{sca, abs} = \frac{3}{4} \sum_i \int \frac{P(r_i) Q_{sca, abs}(r_i)}{r_i} dr_i$$

where $Q_{sca, abs}(r_i)$ is the scattering or absorption efficiency of a particle with radius, $r_i$, and $i$ is the binning index [26]. The ensemble averaged particle asymmetry factor is

$$g = \frac{\sum_i P(r_i) Q_{sca}(r_i) g(r_i)}{\sum_i P(r_i) Q_{sca}(r_i)}$$

The effective dielectric permittivity of the compact, $\varepsilon_{eff}$, from Maxwell Garnett Effective Medium Theory is [27].

$$\varepsilon_{eff} = \frac{\varepsilon_m + 3f \varepsilon_p - \varepsilon_m - \varepsilon_p}{\varepsilon_p + 2 \varepsilon_m - f(\varepsilon_p - \varepsilon_m)}$$

where $\varepsilon_p$ and $\varepsilon_m$ are the dielectric permittivities of the particle and medium components. The single particle scattering and absorption efficiencies and scattering anisotropy factor of different particle sizes are provided in the Supplementary Material.

The Monte Carlo method records the path and termination result of $10^8$ photons from an infinitesimally small beam normal to the compact surface. The reflected, absorbed, and transmitted photons are normalized to the total number of photons. A grid resolution of $dx = 0.1$ μm and $d\theta_{grid} = 5$ μm was used for the axial and radial directions, respectively. The total number of grid elements in the axial and angular directions were chosen to fit the compact thickness, t. The diffuse reflectance and transmittance go to zero as a function of the radius of the layer. The method for obtaining optical spectra of compacts containing particles with a distribution of sizes was verified for particles with a narrow distribution of sizes against compacts embedded with particles with uniform size [12].

The physical appearance of the compacts was simulated by converting the reflectance spectrum to its XYZ tristimulus values, defined by CIE [28], and then into displayable RGB values using the software colour-science, an open-source Python package for color operations [29].

Additionally, the optical properties of the compacts were calculated using the Kubelka-Munk model [30,31]. The Kubelka-Munk model describes the transport of light within a slab using the flux in the forward and reverse directions [32]. The reflectance of the slab representing the compact is
\[
R_{KM} = \frac{1}{a + b \coth bSt}
\]

and the transmittance of the slab is
\[
T_{KM} = \frac{b \csch bSt}{a + b \coth bSt}
\]

where \( t \) is the compact thickness, \( a = 1 + K/S \), \( b = (a^2 - 1)^{1/2} \), and the parameters \( K \) and \( S \) are obtained from the scattering and absorption coefficients as \( K = 2\mu_{abs} \) and \( S = 3(1 - g)\mu_{sca}/4 - \mu_{abs}/4 \) [13]. The absorption of the slab representing the compact from the Kubelka-Munk model is \( A_{KM} = 1 - R_{KM} - T_{KM} \).

3. Results and discussion

3.1. Sintered compacts

The compacts are sintered from either nano- or micron-sized silica powder and have different physical appearance, density, and optical properties (cf. Fig. 1 A). The distinct properties are attributed to the microstructure and post-sintering density. The specimens obtained from micro-silica powders have a more porous composite matrix than those consolidated from nano-silica. The porosity is observed in the relative density, diffuse reflectance, physical appearance, and the microstructure of the compact.

3.1.1. Relative density

The density of each composite layer relative to the density of non-porous silica (2.20 g/cm\(^3\)) indicates that the porosity differs for each compact (Table 1). The compacts obtained from micro-silica powder have a density lower than those consolidated from nano-silica powder. The larger air-silica interface resulting from higher porosity serves to increase the scattering and consequently the diffuse reflectance of the micro-SiO\(_2\) based compacts. This is indeed the case since compacts prepared from micro-silica powder consistently exhibit a larger diffuse reflectance than those prepared from nano-sized silica powder (Fig. 2A).

### Table 1

| Sample          | Density (g/cm\(^3\)) | Relative Density (%) |
|-----------------|-----------------------|----------------------|
| Micro-SiO\(_2\)/0% Si | 2.19                  | 99.4                 |
| /0.5% Si        | 1.98                  | 90.1                 |
| /1.0% Si        | 2.12                  | 96.4                 |
| Nano-SiO\(_2\)/0% Si | 2.18                  | 99.2                 |
| /0.5% Si        | 2.15                  | 97.8                 |
| /1.0% Si        | 2.18                  | 99.3                 |

3.1.2. Physical appearance

Furthermore, the scattering in the visible region manifests in the physical appearance of the compacts (Fig. 1B). The compacts obtained from micro-silica powder are opaque while the nano-silica compact is transparent. The nano-silica based compacts containing Si microparticles are black, which indicates there is intense absorption in the visible region. The absorption is due to the generation of charge carriers from interband transitions at energies above the Si bandgap. On the other hand, the micro-silica/Si compacts are grayish in color due to the enhanced interfacial scattering within the more porous compact.

3.1.3. Microstructure

Scanning Electron Microscopy of the compact surface visualizes and reveals the differences between the microstructure of the nano- and micro-silica compacts. The surface of the specimen consolidated from nano-silica powder is smooth and regular (Fig. 2B). The absence of large gaps and recesses suggests any pores in the nano-silica compact are likely nano-sized. The resulting packing density is very high and close to the bulk density of fused silica. Spatially resolved elemental analysis using energy dispersive X-ray spectroscopy (EDS) indicates that the white specks are silicon particles (Figure A2). The particles are distributed evenly throughout the matrix.

The microstructure is different in the compacts consolidated from micro-silica powder. The micro-silica compact without Si particles synthesized using PECS under identical conditions appears to be fully dense. When silicon particles are included, recesses and gaps form which increase the porosity of the compacts. The particles are unevenly...
distributed throughout the micro-silica matrix and are found predominantly in randomly packed domains (Fig. 2C and D). The observed relative density of the micro-silica compacts (Table 1) is consistent with a compact containing domains of cylindrical packing interspersed with random large holes (See Supplemental Material and Figure A3 for details). The difference in sintering behavior of the Si–SiO₂ composite and pure micro-silica is likely to result from different interaction of the two kinds of materials with PECS current, IR irradiation imposed on the sample during PECS, and the large porosity introduced by Si particles.

The temperature and pressure during the PECS processing did not significantly change the size or shape of the silicon particles. When assumed to have a rectangular shape, the average particle size obtained by SEM image analysis was 2.4 μm × 1.3 μm and 2.5 μm × 1.3 μm for the nano- and micro-silica compacts, respectively. These sizes are slightly smaller than measured by Static Light Scattering (SLS) before the compact preparation in which the mode associated with the distribution of the particle diameters was 3.6 μm.

Both nano- and micron-sized silica matrices of the consolidated samples have an amorphous structure. There are no crystalline peaks detected in the X-Ray diffractograms of the pure silica compacts (Figure A4). Upon the inclusion of silicon particles to the mixture, crystalline peaks are detected in the X-Ray diffractograms. Samples with 0.5% and 1.0% microinclusion content exhibit diffraction peaks at 2θ = 32.42, 54.89, 65.69° corresponding to the characteristic (111), (022), and (113) reflections of bulk Si, respectively. The maximum intensities of the lattice planes increase for the higher volume fraction of silicon.

3.2. Comparison of experimental and calculated spectra

Next, the optical spectra of the silicon/silica compacts are examined. The reflectance has a minimum at short wavelengths (Fig. 1A). Beginning at about 500 nm, the reflectance steadily increases to a plateau at about 1100 nm. The edge of the plateau at shorter wavelength corresponds to the bandgap of Si (1100 nm, 1.1 eV) and is expected behavior as charge carriers are generated due to interband transitions at energies beyond the absorption band edge. Monte Carlo simulations provide information about the interplay between absorption and scattering processes within the compacts of varying thickness and volume fraction. The spectra are calculated for a non-porous compact with well-dispersed spherical particles, which results in some differences with the experimental spectra. The analysis is divided into three spectral regions demarcated by (region I) the reflectance plateau at λ > 1100 nm in which there is strong reflectance and negligible absorption, (region II) the absorption region at λ < 750 nm in which the absorption dominates, and (region III) a transition region between λ = 750 nm and 1100 nm which is characterized by a weakening absorption and growing reflectance.

3.2.1. Region I

First, in the reflectance plateau (region I), the radiative transport within the silica compacts is dominated by scattering from the embedded Si microparticles. The calculated scattering coefficient, μ sca, is large and the absorption coefficient, μ abs, is negligible (109.4 cm⁻¹ and 3 × 10⁻³ cm⁻¹ at 1500 nm, respectively at 1%). The scattering anisotropy, g, is approximately 0.5, and yet despite the scattering being moderately forward, the compacts are strongly reflective because the direction of the incident radiation is quickly randomized due to scattering from the randomly dispersed Si microparticles [12].

The effective medium is derived from independent scattering events from single spherical particles. The scattering energies of an irregular particle are expected to be slightly different than a spherical particle [33]. The experimentally measured reflectance might be less than the calculated reflectance due to particle clustering and irregular morphology in the manufactured compacts. We note that it is not uncommon to model scattering from a distribution of irregularly shaped particles using ensembles of regular model particles such as spheres.

Fig. 2. A) Diffuse reflectance of nano- and micro-SiO₂ compacts without Si particles. Scanning electron micrographs of the surface of the (B) nano-silica and (C, D) micro-silica compacts embedded with Si particles at 1%. The white specks are the silicon particles. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
spheroids, or ellipsoids [26].

The spectra from theory show the magnitude of the reflectance plateau increases when either the compact thickness or particle volume fraction is increased (Fig. 3A and B). The dependence of the total reflectance at \( \lambda = 1500 \) nm on the thickness is shown in Fig. 3C. By elongating the physical path length, i.e. the compact thickness, it becomes more probable that the photon direction has reversed from either a back-scattering event or enough diffuse scattering events. The scattering coefficient is directly proportional to the volume fraction of particles (see Eqn. (1) in Section 2), and the magnitude of the plateau is larger in 1% compacts than in 0.5% due to the larger scattering coefficient. The effect of volume fraction on the magnitude of the reflectance plateau is examined in Fig. 3D. The non-monotonic increase of the reflectance is more pronounced in the thicker compacts. The non-monotonic behavior is consistent with the results from the Kubelka-Munk model. Due to the two-flux simplification and the absence of specular reflectance in the Kubelka-Munk model [34], the intensity of reflectance is stronger in thicker compacts but weaker in the thin compacts compared to the results from the Monte Carlo model. See Eqns. (4) and (5) in Section 2 for details. The Monte Carlo method is more accurate because it includes specular reflectance at the front and rear of the composite.

The diffuse reflectance was not detected beyond 2.5 \( \mu \)m experimentally. The computational modeling predicts broad and intense scattering into the IR, and absorption modes are absent in the calculated reflectance spectra which assume a non-absorbing medium with a refractive index of 1.5. Beyond 2.5 \( \mu \)m, there is expected to be a pronounced effect from the absorption from the Si–O stretching modes within the medium. Absorption by oxides have previously been considered in the shell of semiconductor particles coated with an oxide layer [35,36]. Indeed, FTIR shows strong absorption in this region (Figure A5). Other absorption modes within the silica medium produce dips in the reflectance plateau at 1.39 and 2.20 \( \mu \)m. These features are also present in the compacts without silicon (Fig. 2A).

3.2.2. Region II

Second, at short wavelengths in region II, absorption by the silicon particles becomes significant enough to be a competitive transport mechanism and influence the optical behavior. Intense absorption in the visible region is observed (Fig. 4) as expected from the black color of the compacts due to the interband transitions at energies above the Si bandgap. The total absorption increases with the thickness of the silica compact or the volume fraction of the embedded Si particles. The calculated absorption at 500 nm is examined more closely in Fig. 4C and D, and the absorption plateau is reached for a 1 mm thick compact at 1% volume fraction of Si particles or 0.2% for a 3 mm thick compact. The compacts do not fully absorb due to the specular reflectance at the front air-composite interface, which accounts for about 4% of the intensity. The Kubelka-Munk model does not include specular reflectance and the thick compacts completely absorb the incident radiation for volume fractions greater than 0.25%.

The scattering enhances the absorption by elongating the optical path length and enabling more opportunities for absorption. Despite having a non-zero scattering coefficient, both the experimentally
measured and calculated reflectance decrease in compacts that are either thicker or contain more particles. It is not necessary for \( \mu_{\text{abs}} \) to be larger than \( \mu_{\text{sca}} \) for the absorption processes to dominate the transport. In fact \( \mu_{\text{sca}} \) is as much as to 3.5 times larger than \( \mu_{\text{abs}} \) in this region, and yet the reflectance is less than 9% while the absorption is greater than 20% for compacts greater than 50 \( \mu \)m thick (\( \mu_{\text{abs}} = 36.2 \text{ cm}^{-1} \) and \( \mu_{\text{sca}} = 64.0 \text{ cm}^{-1} \) at 500 nm and 1% Si). The imbalance is due to the nature of the transport processes. To reflect light, the photon direction needs to both reverse and avoid absorption, but absorption can terminate the photon propagation anywhere in the compact.

3.2.3. Region III

Finally, in region III between about 750 and 1100 nm, the calculated \( \mu_{\text{abs}} \) is low but not insignificant. The optical properties transition between the highly reflective region in which the scattering processes dominate (\( \lambda > 1100 \) nm) and the highly absorbing region in which the photons are more likely to be absorbed thereby culling transport (\( \lambda < 750 \) nm). At \( \lambda = 850 \) nm, the reflectance and absorption saturate to a maximum of 16% and 84% in Figs. 3C and 4C, respectively. Notably, the plateau of maximum reflectance is reached in thinner compacts (\( t = 400 \mu \)m) than the plateau of maximum absorption (\( t = 3 \) mm). At this wavelength, compacts thicker than 400 \( \mu \)m increase the absorption but not the reflectance. The diffuse scattering which results in reflectance occurs in the front 400 \( \mu \)m of the compact.

3.3. Effect of particle size distribution

The scattering resonance energies vary with the particle size and its distribution, and the optical properties of compacts containing other size distributions are compared with compacts containing the experimentally measured size distribution (Fig. 5A). The theoretical particle sizes are truncated normal distributions and provided alongside the single particle scattering efficiencies for the particle sizes in Fig. 5B. The reflectance is strengthened by either decreasing the average particle size or including more small particles. Decreasing the average particle size has a more drastic increase on the reflectance than changing the standard deviation and the consequences are discussed for compacts containing 1% Si particles below.

The reflectance increases in compacts containing a smaller average particle size than the experimentally measured mode diameter (3.6 \( \mu \)m). For a fixed volume fraction, the larger particles occupy volume without significantly enhancing the scattering or absorption coefficients employed in the Monte Carlo modeling of radiation transport. See Section 2 for details. Thus, the particle number density increases with a lower average size. This trend is illustrated in the significantly larger scattering coefficients for particles with a smaller average particle diameter than 3.6 \( \mu \)m (Fig. 5C). The more intense scattering coefficient at shorter wavelengths changes the reflectance profile in the compacts containing smaller particles. While the absorption coefficient is also increased for smaller average particle sizes, the absorbance is overcome by the strong scattering and the transmittance remains low in the visible region (Figures A6 and A7). The composites containing smaller particles are expected to be reddish tan color due to the strengthened reflectance of longer wavelengths of the visible region. This appearance was validated in the simulated appearance of the compacts shown in the inset of Fig. 5A. The microstructure will also influence the physical appearance.

Fig. 4. Calculated absorption spectra of silica-silicon compacts of thickness, \( t = 50 \mu \), 100 \( \mu \), 200 \( \mu \), 400 \( \mu \), 1 mm, and 3 mm with A) 1% volume fraction B) 0.5% volume fraction. C) Absorption at \( \lambda = 500 \) nm and 850 nm for different compact thicknesses. D) Absorption at \( \lambda = 500 \) nm for different volume fractions and calculated with either Monte Carlo (MC, solid lines) or the Kubelka-Munk model (KM, dashed lines). See Eqns. (4) and (5) in Section 2 for details of the KM model. The solid lines in C) and D) are drawn to guide the eye. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)
of experimental compacts.

Next, the standard deviation is varied for distributions with an average diameter equal to the mode experimentally measured particle diameter (Fig. 5D). As the distribution broadens, the ripple structure of the scattering coefficients flattens and the magnitude of the scattering coefficient increases as the particle size distribution broadens (Figure A7).

4. Conclusions

PECS is a facile, straight-forward approach to manufacture composites. Unlike other manufacturing techniques, PECS has the potential to produce NIR reflective compacts at large-scale and with a cost-effective method. Silica-silicon particle composite compacts were synthesized using PECS from either nano-silica or micro-silica powder and their optical properties compared with the results from calculations.

Incorporating a small volume fraction of micro-Si particles changes the composites from short wavelength reflectors (Fig. 2A) to long wavelength reflectors (Fig. 1A). Diffuse reflectance of up to 72% can be achieved with silicon particle volume fractions of 0.5% and 1% in 3 mm thick compacts. The specimens obtained from nano-silica powders had a denser and less porous composite matrix than those consolidated from micro-silica. The rapid processing time of PECS limits the undesirable transformations such as crystallization, oxidation, and grain growth.

The broadband NIR reflectance was obtained with a wide size distribution of microparticles. The size distribution affects the reflectance intensity and profile, and composites containing larger particle number densities were shown to have stronger reflectance. Compacts containing small particles changed from black or gray to a reddish tan color. The spectra calculated using Monte Carlo and Kubelka-Munk methods predicted that a significant increase in reflectance can be obtained by lowering the average particle size as opposed to a narrower particle size distribution. However, composites with a narrow size distribution that can selectively reflect a given wavelength region can be exploited for applications in gradient heat flux sensors or detectors.

Given the low dissipation in semiconductor microinclusions, these composites can be used to control the radiative transfer of heat in devices at high temperature. Our ongoing and future work is focused on the development of composites containing bandgap engineered semiconductor particles in multi-layered systems with a graded distribution in a wide range of host materials to enhance radiative transfer mechanisms in targeted applications.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was performed as part of the Academy of Finland project 314488 and QTF Centre of Excellence program (312298, KC and TAN). We acknowledge the provision of facilities and technical support by Aalto University at OtaNano - Nanomicroscopy Center (Aalto-NMC); computational resources provided by CSC - IT Center for Science (Finland) and by the Aalto Science-IT project (Aalto University School of Science); Natural Sciences and Engineering Research Council (NSERC) of Canada (MK); Canada Research Chairs Program (MK); and Compute Canada (www.computecanada.ca).
Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ceramint.2021.02.257.

References

[1] A.V. Kabashin, P. Evans, S. Pankovsky, W. Hendren, G.A. Wurtz, R. Atkinson, P. Pollard, V.A. Podolskiy, A.V. Zayats, Plasmonic nanorod metamaterials for biosensing, Nat. Mater. 8 (2009) 867.

[2] G. Jonsson, D. Tordela, T. Pakizeh, M. Jaysankar, V. Miljkovic, L. Tong, M. P. Jonsson, A. Dmitriev, Solar transparent radiators by optical nanoantennas, Nano Lett. 17 (2017) 6766–6772.

[3] Y. Ma, C. Zagar, D.J. Klemme, D. Sikdar, L. Velleman, Y. Montelongo, L. Velleman, A. Komyama, A tunable nanoplasmonic mirror at an electrochemical interface, ACS Photonics 5 (2018) 4604–4616.

[4] A. Sousa-Castillo, غ. Ameneiro-Prieto, M. Comesaña-Hermo, R. Yu, J.M.-F. Vilaseguriez, M. Pérez-Lorenzo, F. Rivadulla, F.J.G. de Abajo, M.A. Correa-Duarte, Hybrid plasmonic nanoresonators as efficient solar heat shields, Nanomater. 3 (2017) 118–125.

[5] A.V. Miityakov, S.Z. Sapozhnikov, V.Y. Mityakov, A.A. Snarskii, M.I. Zhenirovsky, S. Christiansen, M. Schmid, Integration of plasmonic Ag nanoparticles as a back reflector in ultra-thin Cu (In, Ga) Se2 solar cells, Appl. Surf. Sci. 355 (2015) 800–804.

[6] C. van Lare, G. Yin, A. Polman, M. Schmid, Light coupling and trapping in ultrathin Cu (In, Ga) Se2 solar cells using dielectric scattering patterns, ACS Nano 9 (2015) 9603–9613.

[7] G. Baffou, R. Quidant, Thermo-plasmonics: Using metallic nanostructures as nano-sources of heat, Laser Photon. Rev. 7 (2013) 171–187.

[8] V. Thakore, J. Tang, K. Conley, T. Ala-Nissila, M. Karttunen, Thermoplasmonic response of semiconductor nanoparticles: a comparison with metals, Adv. Theory Simulations 2 (1) (2014), 1800100.

[9] J. Tang, V. Thakore, T. Ala-Nissila, Plasmonically enhanced reflectance of heat radiation from low-bandgap semiconductor microinclusions, Sci. Rep. 7 (2017) 5696.

[10] B.A. Slobick, J.M. Baker, Z. Flom, S. Krishnamurthy, Tailoring diffuse reflectance of inhomogeneous films containing microplatelets, Appl. Phys. Lett. 107 (2015) 141903.

[11] M. Kerker, Scattering by a sphere, in: The Scattering of Light and Other Electromagnetic Radiation: Physical Chemistry: A Series of Monographs, Academic press, 2013, pp. 27–98.

[12] R. Alae, R. Filter, D. Lebr, F. Lederer, C. Rockstuhl, A generalized Kerker condition for highly directive nanoantennas, Opt. Lett. 40 (2015) 2645–2648.

[13] S. Kruk, Y. Kivshar, Functional meta-optics and nanophotonics governed by Mie resonances, ACS Photonics 4 (2017) 2638–2649.

[14] G. Madraiveeran, R. Ramaraj, Gold nanoparticles embedded in silica sol-gel matrix as an amperometric sensor for hydrogen peroxide, J. Electroanal. Chem. 608 (2007) 52–58.

[15] R.F. Cuevas, E. Gunsek, E.H. Selviya, D.Y. Ogata, D. Torikai, C.K. Suzuki, Effect of H2/O2 ratio on the GeO2 concentration profile in SiO2: GeO2 glass preforms prepared by vapor-phase axial deposition, J. Non-Cryst. Solids 273 (2000) 252–256.

[16] D. Hiratsuka, J. Tatami, T. Wakahara, K. Komeya, T. Meguro, Fabrication of transparent SiO2 glass from pressureless sintering of floc-cast green body in air, J. Ceram. Soc. Jpn. 115 (2007) 392–394.

[17] M. Szafar, K. Konopka, E. Bobryk, K.J. Kurzydłowski, Ceramic matrix composites with gradient concentration of metal particles, J. Eur. Ceram. Soc. 27 (2007) 651–654.

[18] Z.A. Munir, D.V. Ouch, M. Ohyanagi, Electric current activation of sintering: A review of the pulsed electric current sintering process, J. Am. Ceram. Soc. 94 (2011) 1–19.

[19] V.K. Singh, M.E. Cura, X. Liu, L.-S. Johansson, Y. Ge, S.-P. Hanners, Tuning the mechanical and adsorption properties of silica with graphene oxide, ChemPlusChem 79 (2014) 1512–1522.

[20] Z. He, R. Tu, H. Katsui, T. Goto, Synthesis of SiC/SiO2 core-shell powder by rotary chemical vapor deposition and its consolidation by spark plasma sintering, Ceram. Int. 39 (2013) 2605–2610.

[21] L. Wang, S.L. Jacques, L. Zheng, MCM-Monte Carlo modeling of light transport in multi-layered tissues, Comput. Methods Progr. Biomed. 47 (1995) 131–146.

[22] E.D. Palk, Handbook of Optical Constants of Solids, Academic press, 1998.

[23] S. Merkakilo, Computer Modeling of Light Scattering by Atmospheric Dust Particles with Spheres and Ellipsoids, Aalto University, 2016.

[24] V.A. Markel, Introduction to the Maxwell Garnett approximation: Tutorial, J. Opt. Soc. Am. A 33 (2016) 1244–1256.

[25] C. CIE, Commission internationale de l’éclairage proceedings, 1931, Cambridge Univ, Cambridge, 1931.

[26] T. Mantsencal, M. Masuderer, M. Parsons, N. Shaw, K. Wheatley, S. Cooper, J. D. Vandenberg, L. Canavan, K. Crowson, O. Lev, K. Leinweber, S. Sharma, T. J. Sobotka, D. Moritz, M. Popp, C. Rane, P. Eszmamortomy, J. Merick, B. Pearlstine, M. Leonhardt, O. Nieni, M. Szymanski, M. Schambach, S. Huang, M. Wei, N. Joywardhan, O. Wagh, P. Redman, J. Goldstone, S. Hill, Colour 0.3.16, 2020, https://doi.org/10.5281/zenodo.3757045.

[27] P. Kubelka, New contributions to the optics of intensely light-scattering materials. Part I, J. Opt. Soc. Am. 38 (1948) 448–457.

[28] M.J.C. van Gemert, A.J. Welch, W.M. Star, M. Motamedi, W.-F. Cheong, Tissue optics for a slab geometry in the diffusion approximation, Laser Med. Sci. 2 (1987) 295–302.

[29] A.B. Murphy, Modified Kubelka-Munk model for calculation of the reflectance of coatings with optically-rough surfaces, J. Phys. D. 39 (2006) 3571.

[30] D.C. Tsarouchis, P. Yia-Ojala, T. Ala-Nissila, A. Silvola, Shape effects on surface plasmons in spherical, cubic, and rod-shaped silver nanoparticles, Appl. Phys. A 122 (2016) 298.

[31] W.E. Vargas, G.A. Niklasson, Applicability conditions of the Kubelka-Munk theory, Appl. Optic. 36 (1997) 5580–5586.

[32] K. Conley, V. Thakore, T. Ala-Nissila, Plasmonically enhanced spectrally-sensitive coatings for gradient heat flux sensors, in: 2018 Progress in Electromagnetics Research Symposium (PIERS-Toyama), IEEE, 2018.

[33] K.M. Conley, V. Thakore, F. Seyyehydayi, M. Karttunen, T. Ala-Nissila, Directing near-infrared photon transport with core/shell particles, AIP Adv. 10 (9) (2020), 095128.