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ABSTRACT
Solar thermal energy systems combined with low-cost thermal storage provide a sustainable, dispatchable source of renewable energy. One approach to increase the attractiveness of these systems is to use high-performing solar transparent, thermally insulating silica aerogel to significantly increase efficiency. Several past works have proposed using these ultra-nanoporous materials to reduce thermal losses in the receiver, but only recently have aerogels reached the high solar transparency necessary to be considered for concentrated solar applications (>97%). However, the durability and stability of optically transparent silica aerogels at the operating conditions of solar-thermal receivers has not been examined. Here, we investigate the high temperature stability of transparent silica aerogel for use in concentrated solar thermal energy applications. Transparent samples (visible transmission >95% at 4 mm thickness) were annealed for several months at 400, 600, and 800 °C to investigate the relative change in nanostructure, solar transparency, and effective thermal conductivity. Results showed that at 400 and 600 °C, the temperature-dependent changes reach a plateau within 30 days of continuous annealing, but at 800 °C, samples are structurally unstable. A simple receiver efficiency model was used to show stable performance at 400 and 600 °C temperatures, even after months of exposure. This work validates that transparent silica aerogels can be used in solar thermal receivers below 800 °C, yielding appreciable increases in efficiency for solar energy harvesting operation.

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INTRODUCTION
In a world that is constantly increasing its energy demands, solar thermal energy conversion has the potential to fulfill a substantial portion of power requirements. Concentrated solar power (CSP) systems use large concentrating optics to focus sunlight onto an absorbing receiver that transfers heat at high temperatures to a working fluid for direct use or electricity generation via a heat engine. Unlike more popular wind and photovoltaic systems, CSP systems can take advantage of low cost and efficient thermal storage to provide energy throughout a 24-h output cycle. By increasing the efficiency of CSP systems, energy can be generated and stored in a way that makes solar thermal harvesting competitive in today’s growing renewable landscape. One approach to achieve high system efficiency is by increasing solar energy absorption and/or suppressing heat loss of the receiver. Transparent, insulating aerogels provide a unique blend of intrinsic properties (heat loss suppression, solar transmission, lightweight, etc.) that have the potential to increase receiver performance with minimal impact on the existing receiver design and cost. The ultra-nanoporous structure of silica aerogel enables both low thermal conductivity and high transparency, even in regimes where radiative heat loss is otherwise dominant. The aerogel structure consists of a cross-linked silica particle backbone supporting a highly mesoporous (2–50 nm) network comprised of aggregated particles, as seen in Figs. 1(a) and 1(b). With a low solid volume fraction and pore sizes smaller than the mean free path of air, the solid and gaseous thermal conductivity of aerogels is very low (less than the thermal conductivity of air at room temperature). The radiative thermal conductivity is also very low due to the high absorptivity of the silica particles in infrared (IR) wavelengths; the particles absorb incident radiation and reradiate in all
FIG. 1. (a) Image and structural representation of an optically transparent silica aerogel fabricated with solar transparency $>97\%$. Small primary silica particles ($<1\ nm$ diameter) aggregate together to form larger secondary silica particles ($\sim 2\ nm$ diameter). These secondary particles bond together to form an interconnected necklace structure that supports a highly mesoporous network. (b) SEM image showing the interconnected structure. Pore sizes vary greatly in the material, but mean pore size is $\sim 10\ nm$. (c) Transmission spectra of a 4 mm thick transparent aerogel sample compared to the AM1.5 solar spectrum.

Solar thermal applications often require the aerogel to reach temperatures in excess of 200 $^\circ$C; therefore, it is important to understand the structural changes that affect performance of the aerogel at high temperatures. High temperature annealing is a simple and effective way to study the structural and performance changes in the material at the upper limit of thermal exposure. Past works have investigated using annealing to optimize performance, but these studies have been limited to temperatures well below the glass transition temperature and/or at time scales far lower than real-world operation in application. Here, we investigate the long-term stability of continued operation at high temperatures by annealing samples at 400, 600, and 800 $^\circ$C and considering the effects on the material structure and performance for solar applications.

METHODS/EXPERIMENTAL PROCEDURE

To investigate the temperature stability of the transparent silica aerogel structure and performance, samples were made into two batches using the method described in Strobach et al. This recipe was chosen for its exemplary solar transparency and a density of $167 \pm 5\ kg/m^3$ that was optimized for applications in linear concentration systems described in Weinstein et al. One sample from each batch was progressively annealed for increasing time at
each of the prescribed temperatures (400°C, 600°C, and 800°C). Additionally, an unannealed reference sample was used as a control from each batch. Characterizing a sample from each batch for each annealing condition reduced the effects of batch-to-batch variation as well as any other anomalies from fabrication. Data were averaged between the two batches for analysis, but we note that values varied by less than 20% between both batches for all data shown here.

Samples were characterized in their initial conditions and then annealed in an oven (Vulcan D-550, Ney) at each of the respective temperatures for times ranging from days to months (depending on the expected level of structural change as estimated from prior works, such as the work of Strobach et al.). At key points in the annealing process, samples were removed from the oven and allowed to cool for ~1 h before characterization. Samples were then placed back into the oven with ~1 h ramp time to reheat to the annealing temperature. Material properties (particularly structural data) were used to evaluate the annealing schedule and adjust or extend time periods between characterization to best probe the material changes. When samples showed at least three consistent data points (<5% fluctuation) for all relevant properties, samples were assumed to be stable (see Fig. S1 of the supplementary material for schedule). We also characterized unannealed reference samples each time an annealed sample was characterized to provide a baseline for anomalies or instrument variations during measurements. These measurements also provided an estimation of repeatability for each characterization.

Structural characterization of the nanostructure was performed by small angle x-ray scattering (SAXS) using a Cu K-alpha x-ray source (SAXSLAB). The scattering pattern was reduced and corrected using SAXSGUI software, and the mean scattering radius was estimated using MC SAS software.22 Area and thickness were measured by image analysis against a known visual reference using ImageJ software.23 The mass of the aerogels was taken on an analytical balance (DV215, OHAUS Discovery DV215) in ambient conditions. Optical properties were measured on an ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometer (Cary 5000, Agilent) on wavelengths from 250 to 2500 nm using a polytetrafluoroethylene coated integrating sphere. The direct radiative transmission and reflection spectra were measured using a Fourier transform infrared spectrometer (FTIR6700, Thermo Fisher) in the wavelength range of 1.5–18 μm.

RESULTS AND DISCUSSION

Densification of the samples was the most obvious indicator of the magnitude of structural change during annealing. Figure 3(a) shows the area shrinkage of each sample with increasing annealing time at the selected temperatures: 400, 600, and 800°C. This area shrinkage provided the most direct and accurate quantification of the sample densification (see Fig. S2 of the supplementary material for density data). As expected, the amount of shrinkage increased with annealing temperature. However, the difference in shrinkage with time between the 400 and 600°C samples and the 800°C samples shows that the densification behavior of the aerogel changed at higher temperatures. At 800°C, not only was the densification rate much higher, but the samples also did not reach a steady state size.

To further study the nanofeature changes, we investigated the average scattering size as measured by SAXS. Average scattering size quantifies the mean radius of both pore and particle features that interact strongly with visible and ultraviolet light. In Fig. 3(b), we see that scattering size change was also highly dependent on the temperature. At 400°C, the average scattering size decreased slightly at first but soon reaches a steady state plateau. The raw scattering curve data indicated that this change was driven by a general decrease in average pore size (see Fig. S3 of the supplementary material). At 600°C, the scattering size increased slightly but then also quickly reached a plateau. As in the 400°C samples, the scattering size change was due to shrinkage of the pore size but also an increase in the average particle aggregation size. At 800°C, scattering size increased drastically with no signs of reaching a steady state despite months of annealing. The relative scattering curves show that at 800°C, the structure experienced an increase in the pore and particle interconnectivity, increased particle scattering size, and decreased pore

![Figure 3](https://example.com/figure3.png)

**FIG. 3.** (a) Absolute area shrinkage of all samples as annealed at 400, 600, and 800°C. Direct measurement of the area of each sample was used to estimate when samples reached a steady structural state as a function of annealing time. Shrinkage amount and rate increased with temperature, but while 400 and 600°C annealing temperatures resulted in a plateaued shrinkage, the samples annealed at 800°C did not reach a steady area over the course of the study. (b) Average scattering size of all samples as determined by small angle x-ray scattering (SAXS) as a function of annealing time. The scattering size reached a stable value in the 400 and 600°C studies, but continued to change at 800°C over the course of the study, confirming that the nanofeature changes in the 800°C study were in a different regime than the stable changes undergone during the 400 and 600°C annealing.
scattering size. These behaviors, along with the shrinkage data, indicated that at 800 °C, the material was already entering its "glass transition" regime and was experiencing radical changes to the nanostructure with continued annealing exposure.

The structural characterization shows that the nanostructure undergoes some change at all annealing temperatures at or above 400 °C. However, for solar applications, it is of utmost importance to consider not only the structural change but also its effect on receiver performance. To best represent the solar collection performance independently of heat-loss suppression, we chose to consider the solar weighted transmission as the figure of merit. We define the solar weighted transmission as the ratio of integral of the transmitted AM1.5 solar spectrum relative to the integral of the incident solar spectrum for a specified material thickness. The total hemispherical transmitted spectrum is integrated over the wavelength range 250–2500 nm.

Figure 4 shows the solar weighted transmission as a function of annealing time. At 400 °C and 600 °C, solar transparency initially increased by 1%–2% (due to the previously discussed initial pore shrinkage) but remained very stable with continued annealing. Conversely, the drastic structural change that occurred during the 800 °C annealing caused a large optical performance degradation (>30% transmission loss) over the course of the study. Within only one month of annealing, performance dropped well below that of traditional glass and continued to monotonically decrease with additional annealing.

Heat loss through the aerogel is another important performance property for solar thermal receiver application. To understand the changes to the heat loss through the aerogel, total effective thermal conductivity of the aerogel was modeled using the radiative transfer equation with the relevant properties measured by IR transmittance, density, and thickness (see Fig. S4 of the supplementary material for details of the IR transmittance). At high temperatures, radiation is dominant, so the hot-side boundary of the aerogel (T_h) was fixed at the respective samples’ annealing temperature (i.e., 400, 600, and 800 °C) to represent a hot thermal absorber at the conditions matching the annealing study. The cold-side boundary temperature (T_c) of the aerogel was calculated based on the energy balance between incoming heat flux from the hot-side and outgoing radiative and convective losses to ambient from the cold side. The emissivity of the aerogel surface was approximated as 1 in the relevant IR wavelengths, and a convective heat transfer coefficient of 20 W/m²K was assumed to represent typical receiver conditions.

Figure 5 shows the calculated total effective thermal conductivity of the annealed aerogels over the course of the study. It is important to note that the value of thermal conductivity varies with varying aerogel thickness because of the nonlinearity of radiative transport, but thermal conductivity was normalized to a standard average thickness of 4 mm (representing the actual value of sample thicknesses within 10%).

The first trend observed is that the effective thermal conductivity increased significantly with annealing temperature. This is primarily due to the radiative component of heat transfer increasing with an increased hot-side temperature (equal to the respective sample’s annealing temperature). By comparing the unannealed reference curves (hollow shapes), we can compare the effects of this radiation component. The second notable trend is that both the 400 and 600 °C studies reached a steady state thermal conductivity very quickly relative to the unannealed samples, but the 800 °C study continued to experience an increase in thermal conductivity. This is due to the continued densification of the 800 °C aerogels that increased the solid conduction portion of the heat transfer, which quickly became a significant mode of heat loss. Solid conduction became responsible for as much as 20% of the total heat loss, compared to only 2%–4% in the unannealed samples (see Fig. S5 of the supplementary material). These trends indicate that the heat suppression of the aerogels reaches a stable state for temperatures less than 800 °C although the operating temperature will affect the relative performance loss of the aerogel for a given hot-side temperature (corresponding to the annealing temperature in this work).
Solar thermal applications require both high solar transmission and low thermal losses; however, the relative importance of these properties (and the significance of their changes during operation) is highly dependent on the configuration and operating conditions. For example, the aerogel solar transparency can increase with annealing, while thermal properties can degrade, but if the optical losses are dominant in a particular receiver setup, it is still favorable to use annealing to increase performance. Therefore, when we consider the stability of the aerogel in solar thermal applications, it is important to consider the effect of property changes on the device performance metrics. In this case, we have chosen to use receiver efficiency to investigate the effects of aerogel thermal stability on receiver performance.

Here, we use a simplified model for receiver efficiency that uses the relevant solar transmission and thermal properties we have presented. Using a 1-D receiver configuration presented in Strobach et al., we can estimate the efficiency of the receiver as

\[
\eta_{\text{rec}} = \tau \alpha - \frac{k_{\text{eff}} (T_H - T_C)}{\eta_{\text{conc}} CG},
\]

where \( \tau \) is the measured solar transmission through the aerogel and \( \alpha \) is the absorber absorptivity in the solar spectrum (assumed to be 1). \( T_H \) is the corresponding annealing temperature of each study, and \( k_{\text{eff}} \) and \( T_C \) values are taken from the model of the thermal properties. The thickness (\( t \)) of each aerogel is taken from measurements. The optical concentration efficiency (\( \eta_{\text{conc}} \)), concentration ratio (\( C \)), and solar irradiance (\( G \)) were selected from the optical configuration of the system. We assumed \( \eta_{\text{conc}} = 100\% \) and chose \( C \) to represent a characteristic system for each of the operating temperatures (400 suns for 400 \( ^\circ \)C, 100 suns for 600 \( ^\circ \)C, and 800 suns for 800 \( ^\circ \)C) achieved in typical concentrator systems. The results of the efficiency model are shown in Fig. 6.

For all temperatures, annealing decreased receiver efficiency by at least 4\%. However, the 400 and 600 \( ^\circ \)C studies quickly reached a stable operating efficiency for months of continuous operation (corresponding to more than 6 months of on-sun operation). This stability degraded at the very high temperatures shown by the 800 \( ^\circ \)C sample efficiencies, where a continuous degradation of efficiency of ~8\% per month was observed. These results show that at temperatures less than 800 \( ^\circ \)C, predictable and reliable performance is possible, provided that the initial effects of the operating temperatures on the material properties and therefore the receiver efficiency are considered.

As a final note, there are many other aspects of the aerogel receiver to consider for stability in long-term applications, such as mechanical stability, condensation effects, and UV exposure. We gave consideration in this work to two common limitations: exposure to water and UV light.

Silica aerogel is naturally hydrophilic, but the small, distributed pores within the surface cannot sustain the induced capillary pressure mismatch when a water-vapor interface is introduced. Any liquid interface is capable of destroying the nanofeatures. One commonly proposed solution is to chemically make the surface conformally hydrophobic by treatment during the wet-gel stage as proposed by Günay et al. The stability of such a hydrophobic coating was investigated by making several samples hydrophobic using hexamethyldisilazane and the process described in Tabata et al. These samples were then progressively annealed until the hydrophobicity degraded completely. At 200 \( ^\circ \)C, the chemical hydrophobicity began to degrade, and at temperatures of 300 \( ^\circ \)C, the surface returned to hydrophilic, as seen in Fig. 6, which agrees with previous studies. This leaves the aerogel vulnerable to damage because it is assumed to be hydrophobic, when in reality, the high operating temperature of solar thermal applications will likely result in a hydrophilic aerogel (see the supplementary material for additional data). However, we believe that water interface and condensation risks can be mitigated in design and assembly with careful consideration for the hydrophobicity of the aerogel. For example, by allowing a space for condensate to collect during the start of on-sun operation, the small amount of water that is desorbed from the aerogel can be kept far enough away from the aerogel to protect it. Another option is to consider bonding aerogel to a thin sheet of protective glass to provide both mechanical and condensation protection.

We also investigated accelerated UV exposure to ensure that there were no adverse effects to the aerogel for extended on-sun exposure. To do this, we placed an aerogel sample under a UV source with a long-wave output peaking at 365 nm at a power of 100 W for...
a 0.01 m² spot size (equivalent to ~250 suns of UV exposure). After running the lamp for 20 h, we removed the sample and characterized the properties (density, scattering size, solar transmission, and thermal transmission). Results show that there was no appreciable change or degradation of any properties for an as-made aerogel (see Table 2 of the supplementary material). This is expected as the base material of our aerogel is silica, which is known to have high UV stability. However, if additional modifications, coatings, or layers (such as the hydrophobic coatings discussed above) are to be used in the design of the receiver, it is important to consider the effects of UV stability.

CONCLUSIONS

Here we showed that transparent silica aerogel was stable for long times at exposure temperatures up to 800 °C, typical of solar thermal applications. At 400 and 600 °C, the nanofeatures experience an initial structural relaxation regime that caused a small increase in solar transparency and thermal conductivity, but these changes plateaued for continued exposure at high temperatures. Conversely, at 800 °C, the aerogel reached a glass transition regime that resulted in large densification of the structure. Properties quickly degraded at 800 °C, and the solar transparency and thermal conductivity reached a regime that made the aerogel unattractive for solar thermal application. Using a simplified concentrated solar thermal receiver model, we investigated the effects of the structural changes to the relevant properties and found that after the structural relaxation of the initial annealing time, the 400 and 600 °C changes to the relevant properties and found that after the structural relaxation of the initial annealing time, the 400 and 600 °C annealed samples had efficiency values that fluctuated by less than 3% per study. The samples annealed at 800 °C did not reach any stable efficiency and continued to degrade with additional annealing time. These results indicate that these transparent aerogels are able to maintain high receiver efficiency for solar thermal applications at operating conditions less than 800 °C.

SUPPLEMENTARY MATERIAL

See supplementary material for additional details on the annealing schedule as well as full datasets for sample density. The supplementary material also contains additional data and discussion of scattering size change and thermal property change with annealing, as well as changes to material properties for hydrophobic treatments and accelerated UV exposure.

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REFERENCES

1. L. A. Weinstein, J. Loomis, B. Bhatia, D. M. Bierman, E. N. Wang, and G. Chen, Chem. Rev. 115, 12797 (2015).
2. National Renewable Energy Laboratory, Renew. Electr. Future Study Renew. Electr. Gener. Storage Technol. 2, 2, 185 (2012).
3. D. Haranath, G. M. Pajonk, P. B. Wag, and A. V. Rao, Mater. Chem. Phys. 49, 129 (1997).
4. S. Svendsen, J. Non-Cryst. Solids 145, 240 (1992).
5. K. McEnaney, L. Weinstein, D. Kraemer, H. Ghaseemi, and G. Chen, Nano Energy 40, 180 (2017).
6. L. Zhao, B. Bhatia, S. Yang, E. Strobach, L. A. Weinstein, T. A. Cooper, G. Chen, and E. N. Wang, ACS Nano 13(7), 7508–7516 (2019).
7. G. Reichenauer, Aerogels Handbook (Springer US, 2011).
8. J.-J. Zhao, Y.-Y. Duan, X.-D. Wang, and B.-X. Wang, J. Phys. D. Appl. Phys. 46, 015304 (2013).
9. A. Soleimani Dorcheh and M. H. Abbasi, J. Mater. Process. Technol. 199, 10 (2008).
10. R. Caps, J. Fricke, and W. Germany, Sol. Energy 36, 361 (1986).
11. A. Emmerling, R. Petricevic, A. Beck, P. Wang, H. Scheller, and J. Fricke, J. Non-Cryst. Solids 185, 240 (1995).
12. M. Tabata, I. Adachi, Y. Ishii, H. Kawai, T. Sunimiyoshi, and H. Yokogawa, Nucl. Instruments Methods Phys. Res., Sect. A 623, 339 (2010).
13. L. Zhao, E. Strobach, B. Bhatia, S. Yang, A. Leroy, L. Zhang, and E. N. Wang, Opt. Express 27, A39 (2019).
14. L. Zhao, S. Yang, B. Bhatia, E. Strobach, and E. N. Wang, AIP Adv. 6, 025123 (2016).
15. A. Norgaard and W. A. Beckman, Sol. Energy 47, 387 (1992).
16. J. Fricke, Sci. Am. 258, 92 (1988).
17. C. J. Brinker and G. W. Scherer, Sol-Gel Science: The Physics and Chemistry of Sol-Gel Processing (Academic Press, 1990), Vol. 555.
18. P. R. Aravind, P. Mukundan, P. Krishna Pillai, and K. G. K. Warrier, Microporous Mesoporous Mater. 96, 14 (2006).
19. Y. Lei, X. Chen, H. Song, Z. Hu, and B. Cao, J. Non-Cryst. Solids 470, 178 (2017).
20. E. Strobach, B. Bhatia, S. Yang, L. Zhao, and E. N. Wang, J. Non-Cryst. Solids 462, 72 (2017).
21. L. A. Weinstein, K. McEnaney, E. Strobach, S. Yang, B. Bhatia, L. Zhao, Y. Huang, J. Loomis, F. Cao, S. V. Boriskina, Z. Ren, E. N. Wang, and G. Chen, Joule 2, 962 (2018).
22. I. Bressler, B. R. Pauw, and A. F. Thünemann, J. Appl. Crystallogr. 48, 962–969 (2015).
23. M. D. Abrámoff, P. J. Magalhães, and S. J. Ram, Biophotonics Int. 11, 36 (2004), available at https://dspace.library.uu.nl/handle/1874/204900.
24. Department of Energy, Solar Energy Technologies Office Funding Opportunity Announcement Supporting Research, 2018.
25. A. A. Günay, H. Kim, N. Nagarajan, M. Lopez, R. Kantharaj, A. Alsaati, A. Marconnet, A. Lenert, and N. Miljkovic, ACS Appl. Mater. Interfaces 10, 12603 (2018).
26. M. Tabata, I. Adachi, H. Kawai, T. Sunimiyoshi, and H. Yokogawa, Nucl. Instrum. Methods Phys. Res., Sect. A 668, 64 (2012).
27. A. V. Rao and M. M. Kulkarni, Mater. Res. Bull. 37, 1667 (2002).