



# Fluorescent impact cavities in a titanium-doped $\text{Al}_2\text{O}_3\text{--SiO}_2$ aerogel: implications for the velocity resolution of calorimetric aerogels

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## Abstract

Silica aerogels have been shown to be superior at capturing hypervelocity projectiles with minimal alteration. On the basis of what is known about the abundance of natural projectiles in low Earth orbit (LEO), aerogel collectors flown in LEO should collect numerous scientifically interesting extraterrestrial dust particles, including interstellar dust grains. However, to date, only a few extraterrestrial dust grains have been found and not a single contemporary interstellar dust grain has ever been identified or analyzed in the laboratory. This lack of success is due to the fact that when using conventional aerogels it is very difficult, if not impossible, to reconstruct the velocity of captured natural projectiles. To address this problem, we are currently developing aerogel collectors/detectors that passively record the kinetic energy of an impacting projectile. In our previous work, we demonstrated that (Gd, Tb)-doped alumina aerogels may transform into a fluorescent phase(s) as a result of the rapid shock heating experienced by the capture of hypervelocity projectiles and that the amount of fluorescence excited, using a UV light source, is an increasing function of the projectile's kinetic energy. However, our previous work did not demonstrate the accuracy of this 'calorimetric' technique in reconstructing the impact velocity of projectiles. In this paper, we report on the production of fluorescent impact cavities in a Ti-doped (5%)  $\text{SiO}_2\text{--Al}_2\text{O}_3$  aerogel monolith that resulted from the capture of  $4.37\text{ km s}^{-1}$   $20\text{ }\mu\text{m}$  glass beads. In addition we demonstrate that the dispersion of the fluorescent response of this aerogel implies that we should be able to reconstruct the velocity of a captured projectile with a resolution of 20% or better.

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## 1. Introduction

Micron-scale particles moving at hypervelocity ( $v \gg 1\text{ km s}^{-1}$ ) are captured in aerogel with minimal damage as compared with other types of collection med-

ia that have been used in space. The low density and nanoscale porosity characteristic of aerogels make them superior at gradually decelerating and stopping micron-sized hypervelocity ( $v \gg$  speed of sound) projectiles with minimal amounts of damage [1]. Since Tsou et al. demonstrated this capability in the late 1980s [2], arrays of silica aerogels have been flown in space and a NASA sample return mission (Stardust) consisting of silica aerogel collectors is expected to return pristine samples of cometary and interstellar dust in 2006 [3]. Various aerogel collectors have been flown in low Earth orbit

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(LEO), in part to characterize the orbital debris environment, but also with the goal of collecting natural micro-meteorites [4,5]. To date, however, only a handful of extraterrestrial dust particles has been isolated and analyzed in these collectors [5] as most of the captured projectiles are expected to be man-made orbital debris.

The composition and dynamic properties (e.g., spatial density, velocities, and trajectories) of the man-made orbital debris population in LEO is itself of considerable interest to satellite makers and is a field of active research (see e.g., [6]). For our purposes, it is important to note that because orbital debris is kinematically bound to the Earth's gravitational field, the velocities with which such debris can impact a collector in LEO have an upper limit.

Extraterrestrial dust grains, that is, interplanetary and interstellar dust grains, captured in LEO could in principle be distinguished from man-made orbital debris if the impact velocity of the captured projectile were known. In practice, however, reconstructing the velocity of a projectile captured in conventional silica aerogels is difficult because the size (cavity length, radius, etc.) of impact cavities has been empirically shown to be weak functions of the kinematic (velocity, kinetic energy) properties of the projectile [7,4,8]. There are theoretical reasons to expect this behavior from aerogels [9]. Thus, extraterrestrial dust grains captured in conventional aerogel collectors in LEO can only be distinguished from orbital debris through the time-consuming chemical analyses of individual particles extracted from these collectors.

The inability of conventional aerogels to unambiguously record impact velocities provided the motivation for our development of calorimetric aerogels [10]. In previous work, we demonstrated that the kinetic energy loss of a captured projectile, which is ultimately deposited as heat, can produce fluorescent impact cavities in Gd:Tb-doped  $\text{Al}_2\text{O}_3$  aerogels. In addition, we demonstrated that the amount of fluorescence, which should be proportional to the amount of aerogel material transformed into this fluorescent phase(s), increases with the kinetic energy ( $E$ ) of the captured projectile. When we quantified the integrated surface brightness ( $S$ ) of individual impacts, we found that, for over four orders of magnitude in kinetic energy, the amount of integrated fluorescence was an increasing function of the kinetic energy and scaled as

$$S \propto E^n, \quad (1)$$

where  $n \sim 2/3$ . The small size of our aerogel samples ( $\sim 1 \text{ mm}^3$ ), however, precluded us from doing a detailed investigation of the signal dispersion.

Ultimately, our ability to distinguish between orbital debris and extraterrestrial dust grains using calorimetric aerogels will rest on their intrinsic velocity resolution ( $\sigma_v$ ). Measurements of this intrinsic property of calori-

metric aerogels have not previously been done despite their importance because this type of measurement requires that a relatively large number of identical impacts be available in a single aerogel monolith.

In this paper, we extend our previous work in two ways: First, we report on the production of fluorescent impact cavities in a Ti-doped (5%)  $\text{SiO}_2\text{-Al}_2\text{O}_3$  aerogel monolith ( $\rho \sim 190 \text{ mg cm}^{-3}$ ,  $\sim 1 \text{ cm}^3$ ). This finding is significant, and is the first report (to our knowledge) that a Ti-doped Si/Al aerogel is capable of being transformed into a fluorescent phase as a result of rapid shock-heating. The Ti-doped  $\text{SiO}_2\text{-Al}_2\text{O}_3$  aerogel that we report on here has been used to make the first measurements of the velocity resolution capabilities of calorimetric aerogel monoliths.

## 2. Experimental

### 2.1. Synthesis

The Ti-doped aluminosilica aerogel was prepared by mixing 3.20 g of tetraethoxysilane (Aldrich), 4.80 g of aluminum di-(sec-butoxide) acetoacetic ester chelate (Alfa), and 0.25 g of titanium diisopropoxide bis(2,4-pentanedionate) with a solution of 1.50 g of deionized  $\text{H}_2\text{O}$  in 6.00 g of acetonitrile (Fisher). This protocol produces a stable sol that was gelled by adding a solution of 0.40 g of glacial acetic acid (Fisher) in 6.00 g of acetonitrile. Gelation took place in less than 5 min at room temperature. The transparent, colorless gel was allowed to age 15 days prior to supercritical extraction with acetonitrile. After placing the sample in the autoclave pressure vessel and sealing the system, it was pressurized to 800 psi with argon and then heated to 295 °C. While maintaining this temperature the pressure was slowly released.

### 2.2. Hypervelocity impact testing and fluorescence imaging

Our aerogel sample was impact tested at the NASA Ames Vertical Gun Range (AVGR) with  $20.3 \pm 1.4 \mu\text{m}$  diameter glass beads that impacted at  $4.37 \text{ km s}^{-1}$ . The presence of fluorescent impact craters was discovered at the Berkeley Biological Imaging Facility. The surface of the aerogel was illuminated using a standard UV light source and filter combination ( $\lambda \sim 365 \text{ nm}$ ) and fluorescence in the visible ( $\lambda \geq 395 \text{ nm}$ ) was recorded using a Zeiss Axiophot microscope with an attached Photometrics Quantix cooled CCD camera.

## 3. Results

The effects of heating on the fluorescent properties of an aerogel may be simulated by baking a portion of it in

an oven. When a portion of the aerogel sample was heated to 1450°C, it sintered into a white, hard, dense monolith. The monolith showed weak (yellow–red) fluorescence under 254 nm illumination and no visible fluorescence under 365 nm illumination. Powder X-ray diffraction data collected from a pulverized portion of the monolith indicated that the major crystalline phase present is mullite,  $\text{Al}_6\text{Si}_2\text{O}_{13}$ . There was also a significant background that suggested the presence of amorphous material in the sample, possibly a glassy phase consisting of residual silica.

In contrast, we observe fluorescent (yellow–red) impact cavities in our sample under 365 nm illumination, as shown in Fig. 1, indicating the presence of a shock-induced fluorescent crystalline phase in the impact cavity. Because of the small amount of fluorescent impact cavity material that is available, identification of this phase is beyond the scope of this paper. Instead, here we focus on the luminescent aspects of this calorimetric aerogel.

### 3.1. Analysis of images

We define the detector signal  $S$  to be the total amount of fluorescence that can be excited and imaged from the surface. In our previous study of a Gd:Tb-doped alumina aerogel, we defined  $S$  to be the sum of the green pixel values that were above a certain threshold after we subtracted a blue fluorescent background. Because the fluorescence of the impacts appears to be multicolored in the titanium-doped aerogel used in this study, we allowed for the possibility that both the fluorescence signal and background channels could be either red (R), green (G), blue (B) or combinations of any of these.

The amount of fluorescence was quantified for a statistically large number ( $N_{\text{impacts}} = 95$ ) of impact craters

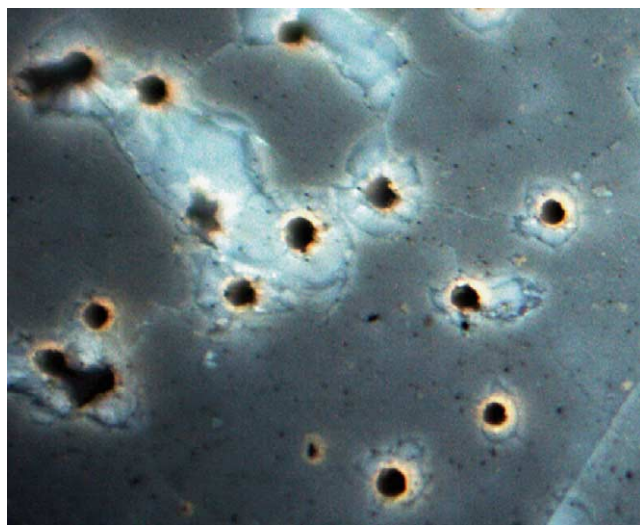


Fig. 1. Fluorescent impact track mouths (contrast enhanced) in Ti-doped  $\text{SiO}_2\text{-Al}_2\text{O}_3$  aerogel system.

on the aerogel's surface in a manner similar to our previous work [10]. To save on computational time, we isolated a patch surrounding each of the impacts for the image analysis. Then, for a particular choice of background and signal channel(s), we produced a background subtracted image  $I_s^*$  by performing the following to each image:

$$I_s^* = I_s - (\langle f_s \rangle / \langle f_b \rangle) I_b. \quad (2)$$

Here  $\langle f_s \rangle$  and  $\langle f_b \rangle$  are the average values of pixels in the signal and background channel(s), respectively in regions of the aerogel's surface that remained unaltered by the impact. Finally, we defined the fluorescence signal  $S$  to be the sum of those pixel values where  $I_s^* > (\langle I_s^* \rangle + N_\sigma \sigma_*)$ . Here  $\langle I_s^* \rangle$  is the average value of  $I_s^*$ ,  $\sigma_*$  is the standard deviation of  $I_s^*$ , and  $N_\sigma$  determines the signal-to-noise ratio that must be exceeded in order for that pixel to be able to contribute to the overall signal  $S$ . In this manner, we ensured that only a change in the color, and not simply an increase in brightness, which would result from a simple increase in aerogel density in the region affected by an impact, would produce a signal in each pixel.

Shock-heated aerogel can fluoresce throughout the optical wavelengths. Therefore, the amount and variation of the fluorescence signal  $S$  is expected to depend on how it is defined. We examined this dependence by analyzing the same set of impacts using a variety of signals (R, G, R + G), backgrounds (B, G, B + G, R + G + B) and values for  $N_\sigma$ . In addition, we explored the effect of using a local region in the vicinity of each impact to provide the background channel values of  $f_s$  and  $f_b$  vs globally imposing a constant background consisting of the average of the local values of  $f_s$  and  $f_b$ . Fig. 2 displays the dependence of  $S$  and the amount of fractional variation,  $\sigma_S/S$ , for  $N_\sigma = 0\text{--}5$ . As expected, the variation in  $\sigma_S/S$  is highest when the background is locally chosen. Note that while the amount of signal  $S$  does depend on how it is defined, the fractional dispersion does not, implying that the fluorescence of the impact cavities has significant red, green, and blue components.

The fractional dispersion appears to be minimized when  $N_\sigma \sim 1$ . For our subsequent discussions on the velocity resolution of the aerogel, we will use the value of  $\sigma_S/S$  that results when  $N_\sigma = 1$ . Fig. 3 displays a particular histogram when  $S = R$ ,  $N_\sigma = 1$ , and the background channel was B. Note the uniformity in the signal  $S$ .

## 4. Discussion

Fluorescence in solids typically results from the interaction of the outer electrons of certain dopants with the crystalline field of the surrounding lattice (e.g., see [11,12]). While we strongly believe that Ti is responsible

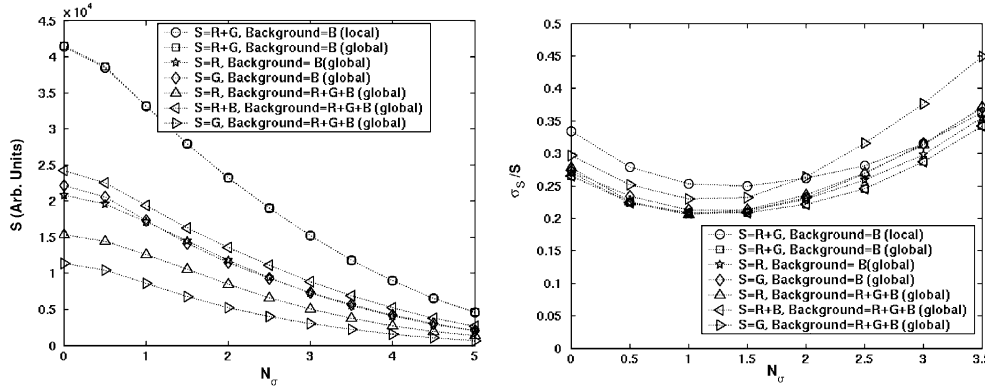


Fig. 2. The dependence of  $S$  and  $\sigma_S/S$  on  $N_\sigma$  for a variety of choices of signal and background channels. The effect of having a local vs global fluorescence background is also shown.

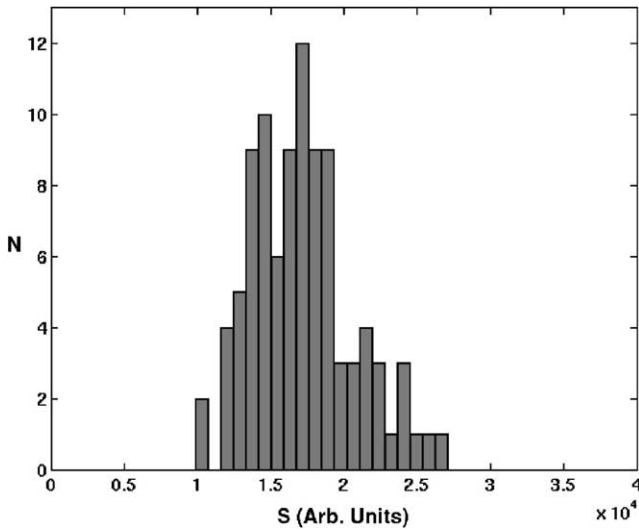


Fig. 3. Histogram of  $S$  for  $S = R$ , Background = B, and  $N_\sigma = 1$ .

for the fluorescence we observe, at this time we cannot identify its oxidation state in the fluorescent impact crater material. The production of fluorescent impact cavities in this Ti-doped  $\text{SiO}_2\text{-Al}_2\text{O}_3$  aerogel, however, does imply that the transformation from the non-fluorescent aerogel phase into a denser fluorescent phase occurs on a timescale that is faster than the time it takes for the impact crater walls to cool down [13].

In general, the response  $S$  (observed signal) of our aerogel collector/detector can be described by a mathematical function of the velocity ( $v$ ), projectile radius ( $r_g$ ), and projectile density ( $\rho$ ). For a statistically large sample of identical impacts, small uncorrelated random deviations of the projectile's velocity, radius, and density (denoted by  $\sigma_v$ ,  $\sigma_r$ , and  $\sigma_\rho$ ) will result in a random distribution of the signal ( $=\sigma_S$ ). Intrinsic detector dispersion ( $\sigma_{\text{noise}}$ ) will also contribute in quadrature. Therefore, the square of the fractional dispersion of the observed signal ( $\sigma_S/S$ ) can be expressed as

$$(\sigma_S/S)^2 = 1/S^2 [(\partial S/\partial v)^2 \sigma_v^2 + (\partial S/\partial r_g)^2 \sigma_r^2 + (\partial S/\partial \rho)^2 \sigma_\rho^2 + \sigma_{\text{noise}}^2]. \quad (3)$$

For a calorimetric aerogel detector whose response,  $S(E)$ , is in the form of Eq. (1), the response to the impact of spherical projectiles can be explicitly written in terms of  $v$ ,  $r_g$ , and  $\rho$  as

$$S = A(\rho r_g^3 v^2)^n, \quad (4)$$

where  $A$  is an arbitrary constant. Assuming that the variation in the density of the spherical projectiles is negligible ( $\sigma_\rho = 0$ ), and using  $\partial S/\partial v = 2n(S/v)$ , and that  $\partial S/\partial r_g = 3n(S/r_g)$ , we find that the relationship between the fractional dispersion of a calorimetric aerogel detector is given by

$$(\sigma_S/S)^2 = 4n^2(\sigma_v/v)^2 + 9n^2(\sigma_r/r_g)^2 + (\sigma_{\text{noise}}/S)^2. \quad (5)$$

When used as a detector, the ability to distinguish between two populations of identical projectiles captured at velocities  $v$  and  $v + \sigma_v$ , respectively, is fundamentally limited by the detector's intrinsic noise level  $\sigma_{\text{noise}}$ . At present, the value of the index  $n$  is not known for the aerogel system under consideration here. However, we can still place some reasonable constraints on the intrinsic velocity resolution,  $\sigma_v$ , of this aerogel. By setting  $\sigma_r$  and  $\sigma_S$  equal to zero in Eq. (5), we can solve for  $\sigma_v/v$  to get

$$(\sigma_v/v) = (1/2n)(\sigma_{\text{noise}}/S). \quad (6)$$

If  $n = 2/3$  and  $\sigma_{\text{noise}}/S \sim 0.2$  (see Fig. 2), we find that  $\sigma_v/v \sim 0.15$ .

However, this value represents an upper limit of the velocity resolution of the technique since we know that the projectiles that impacted the aerogel have a finite size-dispersion. Setting  $(\sigma_r/r_g) \sim 0.09$  (according to manufacturer) and using Eq. (5), we can place a somewhat less conservative estimate on the velocity resolution of the detector. We plot estimates of the detector's fractional velocity resolution ( $\sigma_v/v$ ) as a function of  $n$  in Fig. 4 for both estimates.

Using Eq. (1), we similarly find that the energy resolution,  $\delta E$ , of the calorimetric aerogel technique is given by

$$\delta E/E \sim 1/n(\sigma_{\text{noise}}/S). \quad (7)$$

As before, if  $n = 2/3$  and  $(\sigma_{\text{noise}}/S) \sim 0.2$ , then  $\delta E/E \sim 0.3$ .

Reconstructing the velocity of a captured natural projectile introduces additional uncertainties. If the fluorescence signal, as defined in this paper, is used to find the kinetic energy ( $E = (1/2)mv^2$ ) of a captured projectile, reconstructing its velocity requires that the mass of the projectile be known with reasonable accuracy. How accurately? It is known that natural projectiles captured in aerogel may fragment and ablate as they are slowed and heated during capture [7]. Using an optical microscope, a simple estimate of the size of a captured projectile found at the bottom of the impact cavity (together with a reasonable assumption about its density) yields a lower limit to the projectile's original mass. This lower limit, in turn, can be used to give us an upper limit to the impact velocity of the projectile. For example an underestimate of the mass of a captured projectile by about a factor of 2 leads to an overestimate of the reconstructed velocity by about a factor of  $\sqrt{2}$ , or about 41%. This uncertainty, together with the intrinsic uncertainty introduced by the noise, could result in an overestimate of the velocity by as much as 44% when detector noise is taken into account.

## 5. Conclusion

Underestimating the mass of a captured projectile is clearly the largest source of uncertainty in determining the impact velocity of captured natural projectiles in calorimetric aerogels. However, it should be noted that

the inherent tendency of capturing hypervelocity projectiles is to overestimate the impact velocity of a projectile. Thus, orbital debris that actually impacted at  $6 \text{ km s}^{-1}$  could be misidentified to have impacted at greater than  $8 \text{ km s}^{-1}$ , assuming that we have underestimated the mass by a factor of 2. However, the point of the calorimetric technique is to rapidly identify collected dust grains that are good *candidates* for being extraterrestrial on the basis of their impact velocity. A subsequent direct determination of the projectile's composition could easily rule in or out the extraterrestrial origins of the dust grain [6,5]. Sophisticated, in situ techniques are currently being developed which are capable of measuring the elemental and total mass compositions of captured projectiles with a resolution of about  $\sim 20 \text{ pg}$  [14]. Thus, our example of underestimating the mass of the original projectile by a factor of 2 is probably overly pessimistic, especially for projectiles captured with modest hypervelocities ( $< 8 \text{ km s}^{-1}$ ).

The impact velocities of micron-sized interstellar dust grains captured in an aerogel collector in LEO can be substantially higher (up to  $80 \text{ km s}^{-1}$ ) than the highest projectile velocities obtainable using the light-gas gun facilities at the Ames AVGR. Van-de-Graff accelerators, however, are capable of accelerating sub-micron sized dust grains up to tens of  $\text{km s}^{-1}$ . Future work will include exposures of calorimetric aerogels to Van-de-Graff accelerated dust grains [15]. These tests should provide us with additional information about the capabilities and limitations of calorimetric aerogels in this hypervelocity regime.

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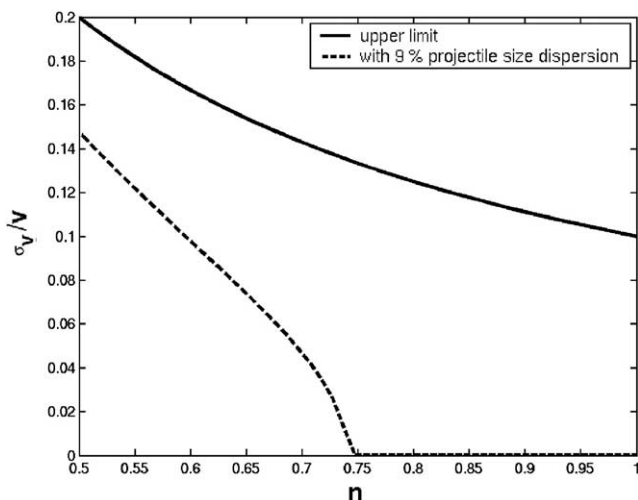


Fig. 4. Fractional velocity resolution of  $\text{Ti:SiO}_2\text{-Al}_2\text{O}_3$  aerogel system.

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