

# Aerosol synthesis of gadolinium iron garnet particles

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Particles of gadolinium iron garnet,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , were produced primarily by an aerosol spray pyrolysis technique starting with solutions of gadolinium and iron nitrates. The as-prepared particles were polydisperse solid spheres. Average diameters in the range 0.05 to 0.8  $\mu$  could be obtained by variation of the initial solution concentration. Larger particles to 2  $\mu$  were created by direct, non-aerosol, pyrolysis of the solutions. Heat treatment caused sintering and particle coalescence and yielded  $\sim 95\%$  garnet phase. The reaction time to create the garnet phase scaled with the square of the particle diameter, the smallest particles transforming the quickest. Magnetic measurements showed bulk behavior for the saturation magnetization, but the coercivity could be varied with particle size with a maximum near the single domain size.

## I. INTRODUCTION

Aerosol synthesis and processing of materials has proven to be a viable and attractive technique. Advantages relative to other synthetic methods include its simplicity, flexibility, and ability to create small particles of high purity. The aerosol spray pyrolysis technique is perhaps the most straightforward of the aerosol methods.<sup>1-11</sup> In this process dissolution of precursor compounds in water is followed by nebulization, drying, and pyrolysis to create small particles. Earlier work of this type has been successful in creating a variety of metal oxide particles.

In this work we have used aerosol spray pyrolysis to create submicron particles of Gadolinium Iron Garnet (GdIG),  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ . The rare-earth garnets are a general class of compounds that display novel and useful magnetic properties and hence are of technological importance.<sup>12-14</sup> In particular, GdIG has potential as a magnetic recording medium due to its magneto-optical Kerr effect properties. Hence it is desirable to create this compound in particulate form for coating carrier substrates. It is also desirable to explore in what manner the magnetic properties of this material might be altered by making the material in particle form. In this paper we describe our synthesis method and characterize these particles with x-ray diffraction and SEM. We also studied the magnetic properties of our particles with a SQUID (Superconducting Quantum Interference Device) and vibrating sample magnetometer. Magneto-optical properties of the particles will be described in a separate paper.

## II. EXPERIMENTAL METHOD

Particles were made in two different ways: aerosol spray pyrolysis and direct drying, pyrolysis, and grinding

of the precursor solutions. Aqueous solutions were made up using appropriate weights of  $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in distilled, de-ionized water with the atomic ratio of Gd : Fe at 3 : 5. The aerosol procedure was described earlier.<sup>10,11</sup> The total solution concentration was varied so that the aerosol mean particle size could be varied. To create aerosol particles the solution was nebulized by a constant output atomizer (Model 3075, TSI, St. Paul, MN) to form a liquid drop aerosol. A typical  $\text{N}_2$  gas flow rate was 1 l/min. The solution was nebulized at a rate of  $\sim 5$  ml/h. This aerosol then passed through a diffusion drier. This drier consisted of a tubular screen 50 cm long and 2 cm in diameter surrounded by the desiccant,  $\text{CaSO}_4$ . We have found that this drying step eliminates the production of hollow spherical particles after the pyrolysis step. The dried aerosol then passed into a tube furnace with inside diameter of 1 cm and length 30 cm. The middle 20 cm of this tube was held at 800 °C. The residence time of the particles in this tube furnace was about 0.5 s. This was sufficient to pyrolyze the dried particles free of nitrogen from the initial nitrate. The particles were collected on cover glass slides by thermophoresis. Our thermophoretic collector consisted of two 6 cm by 12 cm brass plates separated by 1 mm. One plate was held at  $\sim 500$  °C by electric heating, the other at  $\sim 20$  °C by circulating water. The particles were uniformly attracted to the colder plate which was tiled with the cover glasses. We termed these particles "as-prepared." These as-prepared particles were collected and analyzed and then subjected to further heat treatment as described below.

To create large particles the solutions were dried at 80 °C for several hours to a viscous mass. This was then further dried and pyrolyzed at 800 °C for 10 min to a crispy, porous cake. This cake was ground in an agate

mortar and pestle to an amorphous (XRD) powder. These powders were then heat treated the same as the aerosol particles.

Both samples, aerosol and non-aerosol, were analyzed with a scanning electron microscope (SEM), X-ray diffraction (XRD), and SQUID and vibrating sample magnetometers (VSM).

### III. RESULTS

#### A. Morphology and phase evolution

The as-prepared aerosol particles ranged in color from a dull yellow green to a dark olive green. They were polydisperse and spherical in shape, as seen in Fig. 1(a). In all preparations the particles were solid;

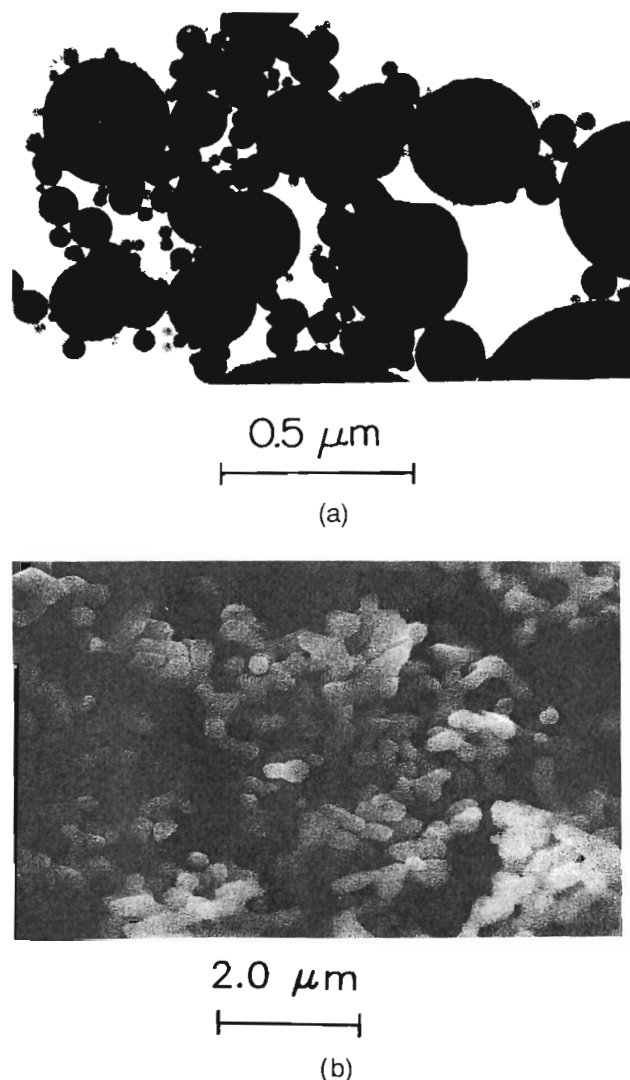


FIG. 1. EM pictures of the aerosol particles. (a) As-received particles from solution concentration of 2.0 wt. %. (b) Same sample as (a) but after heat treatment at 1150 °C for 1 h.

i.e., no hollow particles or shell fragments were seen. XRD showed the as-prepared particles to be amorphous. Analysis of the particle size by SEM inspection yielded a number mean size that increased with solution concentration, as shown in Fig. 2. For the four concentrations shown, the log-log plot in Fig. 2 shows a roughly power law dependence for size with concentration of the form,  $\text{dia.} \propto \text{conc.}^{0.58}$ . If the mean liquid drop size from the nebulizer is independent of concentration, the as-prepared solid particle size should scale as the  $1/3$  power of the concentration.<sup>7</sup> Although no experiments were performed to find the source of this discrepancy, lack of agreement between our results and this prediction could imply the mean liquid drop size from the nebulizer increased with concentration, possibly due to an increase in viscosity of the solution.

Subsequent heat treatment of the as-prepared particles caused mean particle size growth via sintering and particle coalescence, crystallization, and phase evolution. Figure 1(b) shows the heat-treated particles are aggregates of spherules a few spherules per aggregate. Figure 2 also shows that the number mean diameter of these spherules determined by SEM inspection after heat treatment for 1 h at 1150 °C is also roughly power law with concentration with  $\text{dia.} \propto \text{conc.}^{0.3}$ . This should not be construed as corroborating the expected power law dependence with exponent  $1/3$  because heat treatment significantly changes the particle size distribution. We interpret the decline in slope from as-prepared to heat treated in Fig. 2 as a result of the faster coalescence via incorporation during heat treatment of smaller particles into the larger particles when the mean size is small. This is indicated by the lack of small particles in the heat-treated samples, as seen in Fig. 1. In the samples prepared at the lower concentrations, the large number of small particles are rapidly incorporated into larger

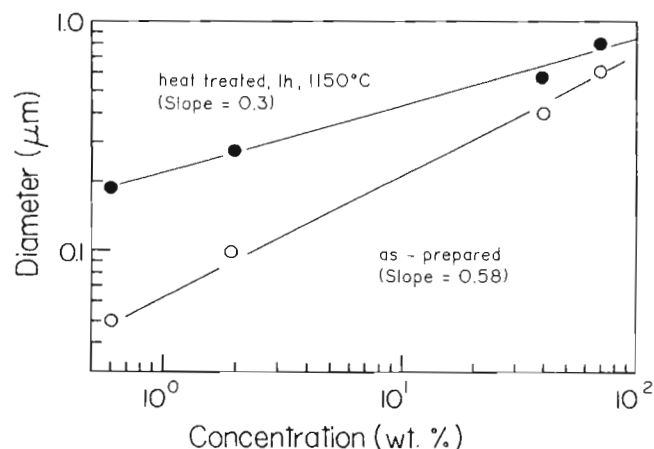


FIG. 2. Aerosol particle diameter as a function of solution concentration. After heat treatment, the diameter is for the spherules that are aggregated together, a few spherules per aggregate [Fig. 1(b)].

particles and the mean size increases significantly. At higher concentration, the as-prepared particles are, on the average, larger; hence incorporation is slower and the mean size increases less than at low concentrations.

Heat treatment crystallized the particles to mixtures of  $\text{Fe}_2\text{O}_3$ ,  $\text{GdFeO}_3$ , and  $\text{GdIG}$ . This compares to work of Multani *et al.*,<sup>15</sup> who made yttrium iron garnet (YIG) powders by a hot-spray process. They found  $\text{YFeO}_3$  and  $\text{Fe}_2\text{O}_3$  appeared first with no detectable YIG phase in the powder, and further heating made the garnet phase appear and increase in concentration. In our case,  $\text{GdIG}$ ,  $\text{GdFeO}_3$ , and  $\text{Fe}_2\text{O}_3$  appeared simultaneously. The weight percent of the garnet phase increased on baking.

Heat-treatment studies were made in order to see the process of conversion to the garnet phase. The particles were heated in air at various temperatures for various times. The phase composition of these particles was then determined with XRD using the method of Klug and Alexander<sup>16</sup> which involves comparison of XRD line intensities. The results are shown in Figs. 3 and 4. There is considerable difference in the rate of formation of  $\text{GdIG}$  phase between the aerosol particles and the non-aerosol particles made by direct drying of the solutions followed by heat treatment. In this comparison, the aerosol particles we used had a mean diameter of  $0.4\text{ }\mu\text{m}$  before heating and  $0.6\text{ }\mu\text{m}$  after heating, while the non-aerosol particles had a mean size of  $2\text{ }\mu\text{m}$ . Some sintering occurred for these particles, but the mean size was kept the same by grinding the particles several times during heat treatment. In Fig. 3 particles were heated at  $1150\text{ }^\circ\text{C}$  for various times. The time required for 90 wt.% conversion to the garnet phase for the aerosol particles was half an hour, much less than that for the non-aerosol particles, which was 15 h. It is interesting that these two samples support

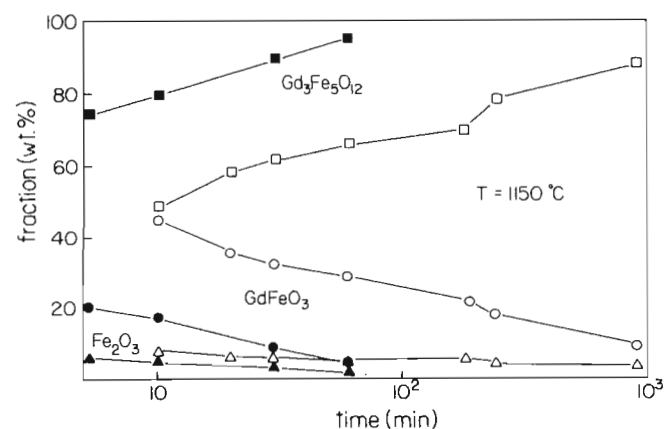


FIG. 3. Fraction by wt.% of the three phases found in the particles as a function of heat treatment time at  $T = 1150\text{ }^\circ\text{C}$ . Solid symbols are for aerosol particles with an as-prepared mean diameter of  $0.4\text{ }\mu\text{m}$ . Open symbols are for non-aerosol particles with mean diameter of  $2\text{ }\mu\text{m}$ .

scaling of the reaction time,  $t$ , with the particle diameter,  $D$ , via  $t \propto D^2$ , since for the aerosol particles  $t/D^2 \approx 190\text{ min}/\mu\text{m}^2$  whereas for the non-aerosol particles  $t/D^2 \approx 225\text{ min}/\mu\text{m}^2$ . Such a scaling of time with size suggests a solid state diffusion mechanism may determine the rate of conversion to the garnet phase. Nonaka *et al.*<sup>8,9</sup> have shown heterogeneities can result from composition segregation during the precipitation step which occurs as the droplets dry. These heterogeneities cause second phases, e.g.,  $\text{Fe}_2\text{O}_3$  and  $\text{GdFeO}_3$ , to form during the pyrolysis step rather than the intended stoichiometric compound, which in our case is  $\text{GdIG}$ . Hence it is reasonable to conclude a similar segregation occurs in our system and a diffusional mechanism is necessary to obtain the conversion to  $\text{GdIG}$ . The reaction time scaling with particle diameter squared,  $t \propto D^2$ , further implies that the size of the heterogeneities must be proportional to the overall dried particle size. This would follow if large-scale heterogeneities developed during drying of the non-aerosol sample. Subsequent grinding would reduce these heterogeneities to the same scale as the particle size.

In Fig. 4 the heat-treatment time was 2 h and the temperature was varied. For the same aerosol particles, the temperature required for 90 wt.% conversion to the garnet phase was  $900\text{ }^\circ\text{C}$ , while at the same temperature, the weight fraction of the garnet phase for non-aerosol particles was less than 70 wt.%. The conversion to the garnet phase in heat treatment follows the relation

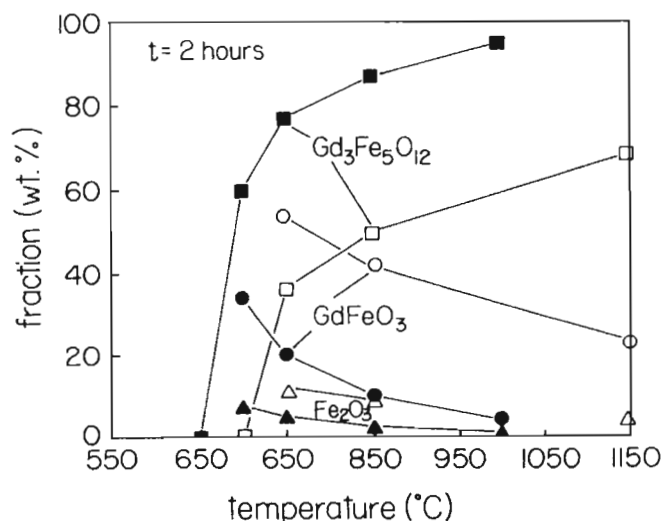
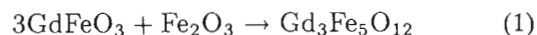


FIG. 4. Fraction by wt.% of the three phases found in the particles as a function of heat treatment temperature for a time of 2 h. Solid symbols are for aerosol particles with an as-prepared mean diameter of  $0.4\text{ }\mu\text{m}$ . Open symbols are for non-aerosol particles with mean diameter of  $2\text{ }\mu\text{m}$ .

This again implies that the aerosol particles were finer grained and more homogeneous, hence more reactive in solid-state reaction.

Figure 5 shows an XRD of the aerosol sample for which the heat treatment was 1150 °C for 1 h in air and the sintered size was 0.3  $\mu\text{m}$ . The GdIG phase is now 95% or better of the total composition, and lines due to  $\text{Fe}_2\text{O}_3$  and  $\text{GdFeO}_3$  have subsided into the noise of the spectrum. Unfortunately, in all samples we found that as the reaction in Eq. (1) neared completion, a line due to an unknown phase occurred at  $2\theta \simeq 69^\circ$ . This line does not match with any known line of any oxide or silicate (our heat treatment boats were silica) of iron or gadolinium. Thus it seems the best we can do is 95% GdIG. As we shall see below, however, this unknown phase does not significantly affect the magnetic behavior.

## B. Magnetic properties

The magnetization and coercivity were measured for particles of mean size 0.3  $\mu\text{m}$ , 0.6  $\mu\text{m}$ , and 2  $\mu\text{m}$  by a SQUID magnetometer and a VSM. The saturation magnetization showed the same behavior for particles of different size, with the specific saturation magnetization at 0 K being 96 emu/g, Curie point at 560 K, and a compensation point at 290 K, as shown in Fig. 6. The saturation magnetization at the compensation point was  $\sim 2$  emu/gr, quite low but not zero, most likely a result of the imperfect yield (GdIG  $\lesssim 95\%$  and the unknown phase). The coercivity vs  $T$  showed a peak at the compensation point, Fig. 7. The reason for this is that if we assume the anisotropy energy is a constant, the coercivity is inversely proportional to magnetization.

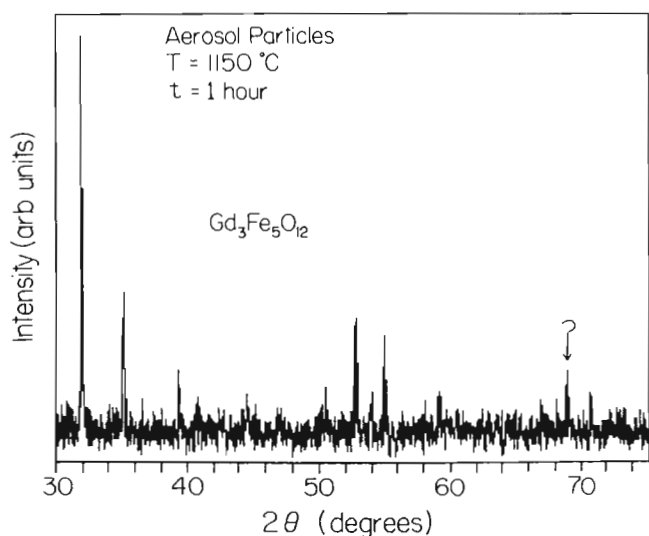


FIG. 5. X-ray diffraction pattern for aerosol particle sample after heat treatment for 1 h at 1150 °C. All obvious lines ( $2\theta = 32^\circ, 35^\circ, 39^\circ, 53^\circ, 55^\circ, 59^\circ$ ) are due to the garnet phase,  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ , except the unknown line at  $2\theta = 69^\circ$  marked with a question mark.

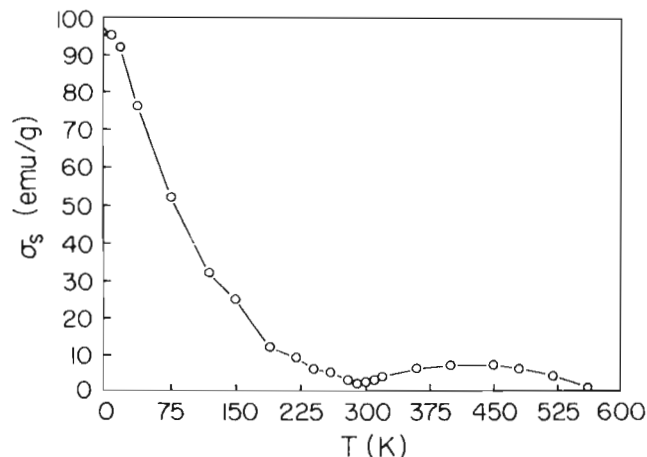


FIG. 6. Saturation magnetization versus temperature for aerosol particles of mean diameter 0.6  $\mu\text{m}$  after heat treatment at 1150 °C for 2 h. This result is typical of all particles with sufficient heat treatment to yield the garnet phase in excess of 90 wt. %.

Thus when magnetization reaches a minimum at the compensation point, the coercivity goes to its maximum. All this behavior is very similar to that found in the bulk material,<sup>12,13</sup> hence no size effect is present here. The coercivity, however, showed significant size effect. Figure 8 shows the relation between coercivity and mean particle size at 290 K. The maximum in coercivity should correspond to when the diameter equals the single domain size, and the coercivity should decrease with diameter both above and below this size.<sup>17</sup> Our results are consistent with the theory and indicate that the critical size for single domain particles for this material is very roughly 0.6  $\mu\text{m}$ . These results are valuable in that they

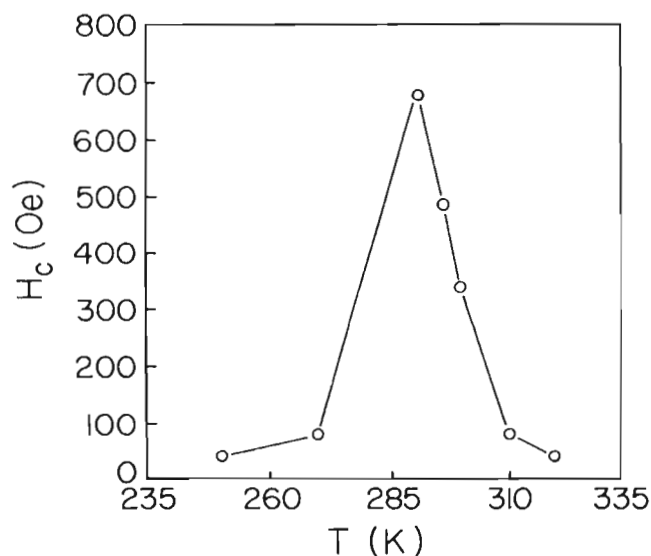


FIG. 7. Coercivity as a function of temperature for 0.6  $\mu\text{m}$  mean diameter particles.

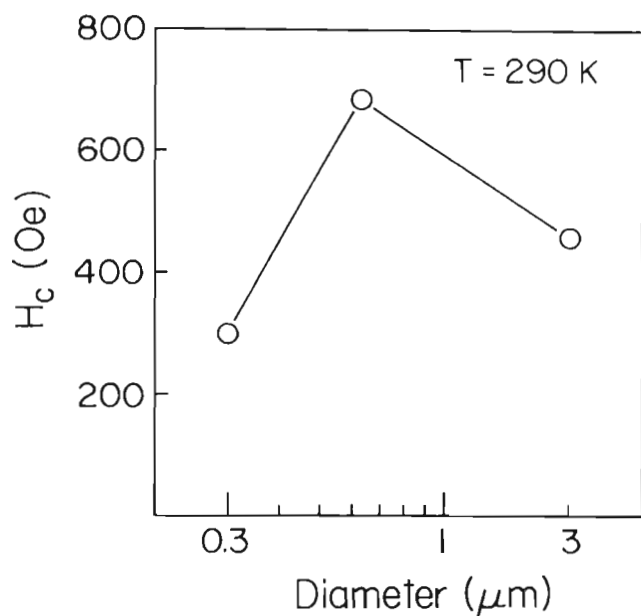


FIG. 8. Coercivity at  $T = 290$  K as a function of particle size.

demonstrate our ability to create particles of any, within a range, coercivity we may desire. Furthermore, this can be done without altering other desirable magnetic properties.

#### IV. CONCLUSION

Particles of Gd-Fe-O were prepared by aerosol spray pyrolysis and a simple milling-sintering method. Particle sizes between 0.05 and 2  $\mu\text{m}$  were obtained. Heat treatment converted this mixture of  $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ,  $\text{GdFeO}_3$ , and  $\text{Fe}_2\text{O}_3$  into the garnet phase ( $\text{Gd}_3\text{Fe}_5\text{O}_{12}$ ) with purity of ca. 95% in weight. The saturation magnetization, Curie temperature, and compensation temperature were size independent and the same as the bulk. The coercivity could be varied with size. This was explained in

terms of a transition from single domain to multidomain behavior, with a domain size of roughly 0.6  $\mu\text{m}$ .

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