were purchased from Polymer Source Inc. and were used as received. PS-*b*-PMMA diblock copolymers having three different molecular weights were used. The characteristics of those block copolymers are as follows: M_n = 51 200, PS block fraction = 0.49 wt.-%, polydispersity index (PDI) = 1.06; M_n = 86 500, PS block fraction = 0.54 wt.-%, PDI = 1.08; and M_n = 143 500, PS block fraction = 0.51 wt.-%, PDI = 1.09. The M_n of the PMMA block was 70 700 and M_n of the P^{t}BuMA block was 84 800 in PMMA-*b*-P*t*BuMA with polydispersity of 1.18. All the homopolymers used in this study were obtained from Aldrich Chemical Company, Inc., and (except for HEMA) were precipitated twice from methylene chloride into methanol for purification. For the purification of HEMA, precipitation from methanol with hexane/methylene chloride (1:1) was carried out twice.

Film Preparation: 0.2 g of polymer was dissolved in 10 mL toluene and poured into an aluminum petri dish with a diameter of 5 cm. The solution was dried in ambient conditions overnight, then dried on a hotplate at 50 °C for 1 day, and finally dried completely in a vacuum oven at 100 °C for 2 days. The thickness of the films was about 100 μm.

TEM: The films were embedded in visible-light curable resin, D-800 (JEOL DATUM Co. Ltd.), and were cured by irradiating with the light from a xenon lamp source through a UV cut filter at 100 mW/cm^2 for 5 min. The films were microtomed to give a thickness of 50 nm at room temperature. The Carl Zeiss EM 902 was operated at an accelerating voltage of 80 kV, and the images were recorded using the Imaging Plates system, FDL5000 (Fuji Photo Films Co. Ltd.). The number-average diameter of the clusters was calculated with image processing software: Ultimage Pro 2.6 (Graftek France). More than 200 particles were counted and individual diameters were assigned to those circles with equivalent area.

UV-vis Absorption Spectroscopy: Measurements were carried out on a Shimadzu UV-2500PC. The 50 μm films prepared by solvent casting as mentioned above were used.

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[1] L. Bronstein, M. Antonietti, P. Valetsky, in *Nanoparticles and Nanostructured Films* (Ed: J. H. Fendler), Wiley-VCH, Weinheim **1998**, Ch. 7.
[2] R. Saito, S. Okamura, K. Ishizu, *Polymer* **1992**, *33*, 1099.
[3] T. Hashimoto, M. Harada, N. Sakamoto, *Macromolecules* **1999**, *32*, 6827.
[4] a) Y. N. C. Chan, R. P. Schrock, R. E. Cohen, *Chem. Mater.* **1992**, *4*, 24. b) Y. N. C. Chan, G. S. W. Crig, R. P. Schrock, R. E. Cohen, *Chem. Mater.* **1992**, *4*, 885. c) B. H. Sohn, R. E. Cohen, *J. Appl. Polym. Sci.* **1997**, *65*, 723.
[5] a) K. Esumi, T. Tano, K. Meguro, *Langmuir* **1989**, *5*, 268. b) T. Tano, K. Esumi, K. Meguro, *J. Colloid Interface Sci.* **1989**, *133*, 530.
[6] M. E. Gross, A. Appebaum, P. K. Gallagher, *J. Appl. Phys.* **1987**, *61*, 1628.
[7] M. Kunz, K. Shull, *Polymer* **1993**, *34*, 2427.
[8] T. P. Russell, G. Coulon, V. R. Deline, D. C. Miller, *Macromolecules* **1989**, *22*, 4600.
[9] A. M. Mayes, T. P. Russell, P. Basseau, S. M. Baker, G. S. Smith, *Macromolecules* **1994**, *27*, 749.
[10] Y. Nakao, *J. Colloid Interface Sci.* **1995**, *171*, 386.
[11] Y. Nakao, *Chem. Lett.* **2000**, 766.
[12] The surface tension of poly(*n*-butyl methacrylate) (31.2 dyn/cm at 20 °C) is lower than that of PS (41.1 dyne/cm). Therefore, the P^{t}BuMA block is expected to be located at the surface: S. Wu, *Polymer Interface and Adhesion*, Marcel Dekker, New York **1982**, Ch. 5.
[13] M. T. Reetz, M. Maase, *Adv. Mater.* **1999**, *11*, 773.

Colloidal Ellipsoids with Continuously Variable Shape**

By *Edwin Snoeks*, *Alfons van Blaaderen*, *Teun van Dillen*, *Carlos M. van Kats*, *Mark L. Brongersma*, and *Albert Polman**

Colloidal particles play an important role in studies of self-assembly and phase behavior, and can find many applications in practical materials with interesting optical properties. The synthesis of colloidal model suspensions is well explored and understood for a wide variety of inorganic materials.[1] However, most of the model systems with a narrow size distribution consist of spherical particles. It appears very difficult to synthesize *non-spherical* particles such as oblate and prolate ellipsoids with low polydispersity.[2] A system of optically transparent ellipsoidal colloids with an adjustable aspect ratio would be ideal to investigate the effect of anisotropic particle shape on phase behavior or optical properties.[3–5] In this communication we report a novel method for synthesizing a new class of inorganic ellipsoidal colloids that exploits a combination of colloidal chemistry[6,7] and ion-irradiation techniques.[8] We find that monodisperse silica and zinc sulfide microspheres show a dramatic anisotropic plastic deformation[9,10] under 4 MeV Xe ion irradiation that can be precisely tuned by varying the ion fluence. Both oblate and prolate particles are made. We show that the deformed ellipsoids can be redispersed into a stable suspension, and preliminary indications of nematic liquid-crystalline ordering are found.

Two dispersions of colloidal silica (SiO_2) spheres in ethanol, with different diameters, were synthesized using techniques described elsewhere.[6] Drops of a dilute dispersion were placed on the clean surface of a Si(001) substrate, after which the ethanol solvent was left to evaporate. In Figure 1a a scanning electron microscopy (SEM) image is shown of the silica spheres on the Si surface, viewed at normal incidence to the substrate. The two different particle sizes are easily distinguished, and the diameters are sharply centered around 290 and 1030 nm, with a relative polydispersity in size of <2 %.

Next, the particles were irradiated with 4 MeV Xe^{4+} ions with the sample surface held at an angle of +45° with respect

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to the direction of the ion beam, as indicated in the schematic inset in Figure 1. Figures lb–d show SEM images taken after irradiation to a fluence of 3×10^{14} ions/cm^2. The images were obtained using different sample tilt angles in the microscope. The three (almost) orthogonal projections provide a full identification of the particle shape after irradiation: expansion is observed in the plane normal to the direction of the ion beam, and contraction in the direction of the beam. In Figure 1b these spheroids are viewed along the direction of the ion beam, i.e., at a +45° tilt angle as indicated in the schematic inset. In this particular projection, the spheroids appear circular. The dashed circle represents the circumference of unirradiated spheres. The projected diameters of both the large and small particles have increased by 24 %. The two images taken perpendicular to the ion beam, Figures 1c and d, show the elliptically shaped side views of the spheroids. The cross-sectional size of the deformed particles along the direction of the ion beam decreased with respect to the original diameter by about 35 %.

Experiments as described above were performed for various Xe ion fluences ranging from 3×10^{13} to 8×10^{14} ions/cm^2. Figure 2 shows the average transverse and longitudinal diameter of the spheroids as obtained from SEM micrographs as a function of fluence, for the large (Fig. 2a) and small (Fig. 2b) particles. The deformation increases monotonically with fluence and the aspect ratio of the most strongly deformed spheres in Figure 2 is 3.11 ± 0.13. The drawn line corresponds to a linear increase in the transverse particle diameter with fluence, while the dashed curve shows how the longitudinal axis must shrink if the volume of the spheroids were to remain constant. Both curves describe the data quite well, indicating that the volume of the particles does not significantly change during the deformation process. The curves shown in Figures 2a and b for the large and small particles are identical, apart from a size scaling factor. This implies that surface tension does not affect the particle deformation. We have performed deformation experiments using different ion fluxes in the range $3–8 \times 10^{10}$ cm^{-2}s^{-1}, and found that the total deformation for a given total ion fluence is independent of the ion flux used.

The particles shown so far have all been obtained using 4 MeV Xe^{4+} ion irradiation at 90 K. We have also studied beam-induced deformation of silica spheres at room temperature. We found that the particles deform in the same way as at 90 K, but at a rate that is slower by about a factor of four. This agrees well with measurements of the temperature dependence of the deformation rate derived from mechanical stress measurements on planar silica films irradiated at 4 MeV.[11]

On a microscopic scale, the anisotropic deformation phenomenon can be viewed as the result of the high electronic

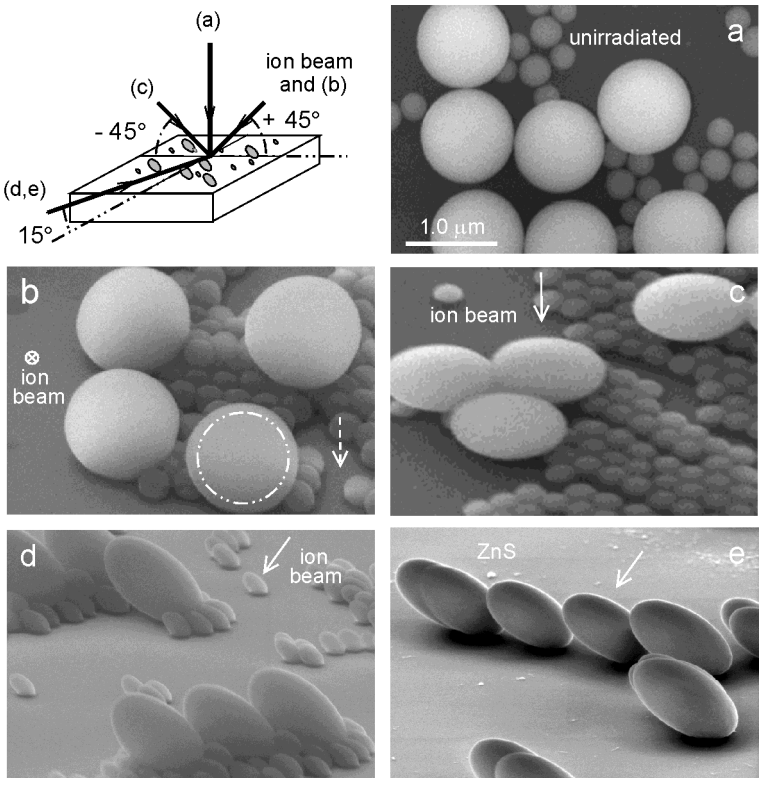

Fig. 1. Scanning electron microscopy images of: a–d) silica and e) zinc sulfide particles on a silicon substrate. a) Top view (0° tilt) of as-deposited silica spheres with two different diameters. b–d) Silica spheroids that have formed after 4 MeV Xe irradiation at a fluence of 3×10^{14} cm^{-2}, at an angle of 45° relative to the surface normal, at 90 K. The ion-beam direction and the different viewing angles are indicated in the schematic inset. The dashed arrow in (b) indicates the direction of the subsequent irradiation performed to obtain the prolate particles shown in Figure 3. e) Zinc sulfide microspheres irradiated with 5×10^{14} Xe/cm^2 at an angle of 45°. The particles were irradiated with a fluence of 5×10^{14} cm^{-2} at 90 K, at an angle of 45°. All images (a–e) are taken at the same magnification.

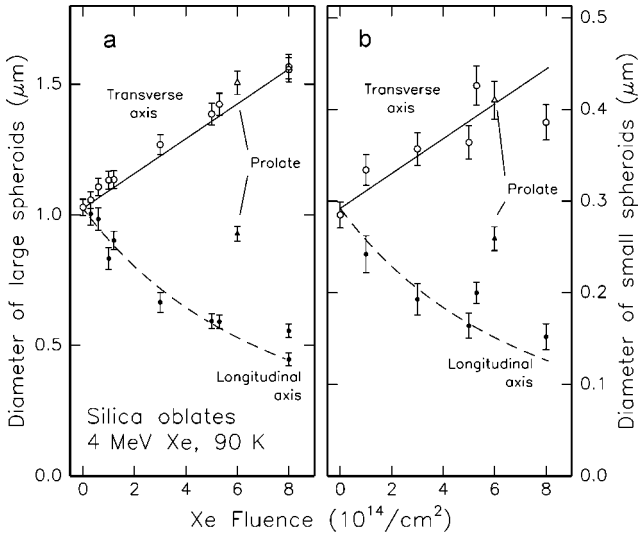

Fig. 2. Transverse and longitudinal diameters of a) large and b) small silica spheres as a function of 4 MeV Xe^{4+} irradiation fluence. Circles correspond to oblate ellipsoids, and triangles to prolate ellipsoids made using two orthogonal irradiations. The line drawn through the data for the transverse axes is a linear fit, the dashed line is a calculation derived from the drawn line assuming the particle volume remains constant with fluence.

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energy deposition (approximately 2 keV/nm) by the 4 MeV Xe ions. Due to the low directional straggle in the ion trajectory, a cylindrically shaped narrow thermal spike evolves around the ion track in the silica with a temperature of a few thousand Kelvin.[12,13] Plastic relaxation of the local shear stress induced by thermal expansion of this hot cylindrical region can result in plastic deformation perpendicular to the cylindrical axis. The observed macroscopic deformation is the result of the integrated effect of a large number of microscopic single ion impacts. Note that at a fluence of 7×10^{14} ions/cm^2 each micrometer-sized particle has been impacted by some 10^7 Xe ions. Over such large numbers any statistical variations are expected to average out, so that the deformed particles are expected to be very monodisperse in both size and shape.

To prove that the deformation is indeed the result of the anisotropic nature of the thermal spike around the 4 MeV ion track, experiments were also performed using 500 keV Xe^{4+} ions.[14] The energy loss rate at this energy is roughly equal to that for 4 MeV, but in this case atomic collisions rather than electronic energy loss dominate the energy deposition. This leads to a much higher lateral ion straggle and hence a less anisotropically shaped excited region. Indeed, no plastic deformation of silica colloids was observed after irradiation at an energy of 500 keV, even to a fluence as high as 1×10^{16} cm^{-2}.

It is interesting to note that while a linear increase in the transverse diameter of the spheroids is observed in Figure 2, an exponential growth of the transverse lengths with fluence would be expected if the deformation rate (per ion) was constant with fluence. This implies that the deformation rate decreases with ion fluence. To account for the behavior observed in Figure 2 we have to assume that the deformation strain per ion gradually decreases from 6.6×10^{-16} cm^2/ion to 4.3×10^{-16} cm^2/ion for the fluence range studied. This change with fluence may be due to a structural or compositional change of the silica during ion irradiation.[15]

An illustration of the reproducibility and versatility of the ion-irradiation technique is that it can also be used for the synthesis of prolate ellipsoids. First, oblate particles were made from originally 1030 nm diameter silica spheres by 4 MeV Xe^{4+} irradiation to a fluence of 3×10^{14} cm^{-2} at an angle of +45°, similar to what is shown in Figures 1b–d. The particles were then again irradiated with 4 MeV Xe^{4+} ions to a fluence of 3×10^{14} cm^{-2}, now with the sample tilted at –45°, i.e., orthogonal to the direction of the first irradiation. This is indicated by the dashed arrow in Figure lb. Figure 3 shows SEM images of these doubly irradiated particles. In the image of Figure 3a, taken using the same sample orientation as in Figure 1b, the particles appear elliptical. The same is found in SEM images taken at other sample tilt angles within the plane expanded by the two ion beam directions. Figure 3b shows the same sample, imaged in a direction that is almost normal to both of the two ion beam directions (75° off the surface normal, as in Fig. 1d). From this angle of view the particle projection is close to circular. Therefore, it can be concluded that the ellipsoids in Figure 3 do indeed have a prolate shape. The total ion fluence used to form these prolate ellipsoids was 6×10^{14} cm^{-2}, and the transverse and longitudinal diameter of the particles are also included in Figure 2 (triangles). Note that the transverse diameter for the prolate ellipsoids follows the trend observed for the oblate ellipsoids irradiated at the same total ion fluence. This further confirms that the deformation phenomenon is beam-directionally anisotropic, and that a high level of shape control can be achieved. Clearly, repeated irradiation from different directions can be used to create much more complex shaped particles than ellipsoids as well.

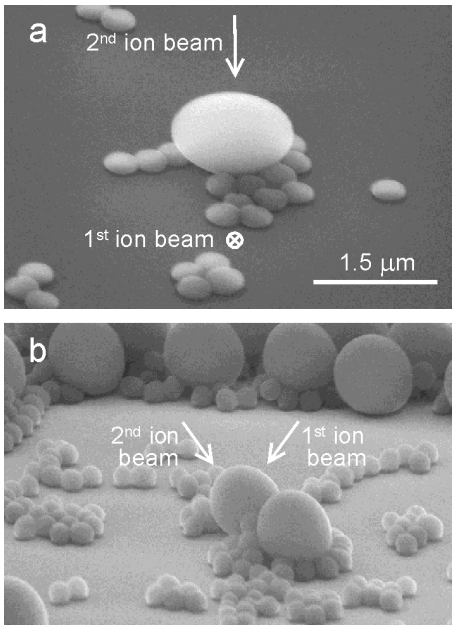

Fig. 3. Prolate ellipsoids: SEM images of silica particles such as those shown in Figure 1a–d, after an additional 4 MeV Xe^{4+} ion irradiation to a fluence of 3×10^{14} cm^{-2} at an angle orthogonal to the first irradiation. a) View along the direction of the first ion irradiation (+45° tilt). b) View almost perpendicular to the two ion beams (same orientation as in Fig. 1d).

To investigate the anisotropic deformation effect on a material other than silica, we performed experiments on colloidal zinc sulfide (ZnS) spheres. These particles can be made with a narrow size distribution, are spherical (diameter 1.17 μm), and consist of aggregates of cubic sphalerite nanocrystals.[16,17] Figure 1e shows an SEM image of these ZnS particles after 4 MeV Xe^{4+} irradiation. As can be seen, these ZnS microspheres are deformed into spheroids as well, with an aspect ratio of 2.2 ± 0.2. As these ZnS particles have a relatively high refractive index, several uses of these deformed particles in optical applications can be envisioned. For example, it has been shown that an oblate microresonator shows strongly improved lasing properties compared to a spherical resonator.[5] When combined with methods that allow control over the orientation and symmetry of two- and three-dimensional colloidal crystals[17,18] the particle deformation technique will also provide an important additional degree of freedom to tune optical phenomena in (thin) photonic crystals. In fact, optical band structure calculations show that, for a given particle asymmetry, photonic crystals composed of spheroids can have larger bandgaps than those composed of spheres.[19]

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We have also performed preliminary investigations of the phase behavior of suspensions of ellipsoidal colloids. To this end, silica spheroids with an aspect ratio of 2.75 ± 0.11 were brought back into ethanol suspension by ultrasonic treatment. A stable suspension of deformed silica particles in solution was obtained and light scattering confirmed that the spheroids were redispersed as single entities. Figure 4 shows a SEM image of a structure formed by these spheroids after they were concentrated by slowly drying the dispersion on the surface of a Si substrate. The figure clearly shows that the particles have dried into a nematic-like structure with clear directional order (with the director pointing out of the plane of the image) and no positional order. Close to the edge of the structure some of the spheroids have a different orientation (see, e.g., the arrow in Fig. 4). This arrangement does not only show that (the majority of) the spheroids have indeed been suspended as individual particles, but also gives strong indications that concentrated dispersions of these spheroids will form a nematic, colloidal liquid-crystalline phase. Computer simulations predict that oblate ellipsoids with an aspect ratio of 2.75 and higher can form such a nematic phase.[4] Nematic–isotropic phase transitions in dispersions of hard plate-like colloids have been observed only recently for a system of gibbsite platelets.[20] However, because of their relatively high size and shape polydispersity and hexagonal shape, comparison of the phase behavior of such particles with computer simulations is much more difficult than for the ellipsoidal particles made using the ion-irradiation technique.

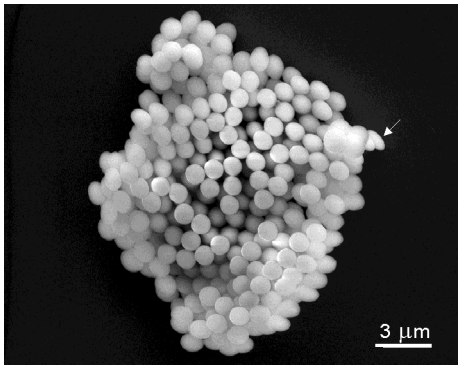

Fig. 4. SEM image of a nematic-like arrangement of oblate silica spheroids (aspect ratio 2.75 ± 0.11), in which the particles show directional ordering but no positional ordering. Computer simulations predict a nematic phase for particles with this aspect ratio for sufficiently high density. Silica spheroids were obtained by 4 MeV Xe^{4+} irradiation of 1030 nm diameter silica spheres at an ion fluence of 6×10^{14} Xe/cm^2. The irradiation temperature was 90 K, and the angle of incidence 45°. A low surface coverage (< 1 %) and non-perpendicular irradiation conditions were chosen to avoid any interaction between deforming particles. After irradiation the particles were dissolved in an ethanol suspension by ultrasonic treatment. This solution was then slowly dried on a silicon substrate. The arrow indicates a spheroid along the edge of the cluster that shows no ordering but gives an impression of the size aspect ratio.

In summary, the combination of chemical synthesis and ion-irradiation techniques makes it possible to fabricate a new class of colloidal ellipsoids with continuously variable shape. Several applications in photonic materials can be envisioned, and a possible application in the assembly of liquid crystals is shown. The particle yield of this new method is relatively low, but it is comparable to that for the fabrication of other anisotropic model systems such as tobacco mosaic viruses or prolate polystyrene ellipsoids made by polymer stretching. To optimize the particle density while avoiding interaction between touching particles a patterned template could be used. The particle yield could be further enhanced by using an automated particle feed-through system. We also expect that much more efficient anisotropic deformation can be achieved by using higher-energy ion beams.

Experimental

Colloidal Synthesis: Silica microspheres were synthesized through hydrolysis and condensation reactions from tetraethoxysilane as described in the literature [6]. ZnS microspheres were made using a similar method to that described elsewhere [16].

Scanning Electron Microscopy: This was performed using a Philips XL30 FEG operated at 10 kV.

Ion Irradiation: A 1 MV van de Graaff accelerator was used, and Xe^{4+} ions were generated in a Penning ion source. The ion beam was electrostatically scanned to homogeneously irradiate the entire sample. The beam flux was in the range 3–8 $\times 10^{10}$ ions/cm^{2}s. The Si substrate was tightly clamped against a copper sample stage and cooled to 90 K using liquid nitrogen. The base pressure during ion irradiation was 5×10^{-7} mbar. The projected mean ion range of 4 MeV Xe ions into silica is around 1.7 μm.

Resuspension of Irradiated Particles: These particles were obtained by 4 MeV Xe^{4+} irradiation of a carbon-coated glass slide about 1 % covered with 1030 nm diameter silica spheres. The ion fluence was 6×10^{14} cm^{-2}, the irradiation temperature 90 K, and the angle of incidence 45°. The low coverage and non-perpendicular irradiation conditions were chosen to avoid interaction between deforming particles. By ultrasonic treatment the irradiated particles did detach easily from the surface while the carbon layer did not detach, most probably as a result of cohesion enhancement due to ion-beam mixing.

Optical transmission measurements were made under normal incidence, using a Varian Cary 500 spectrophotometer employing a white light source, a grating spectrometer, and photomultiplier and Ge photodetectors.

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[1] E. Matijevic, *Langmuir* **1994**, *10*, 8.
[2] C. C. Ho, A. Keller, J. A. Odell, R. H. Ottewill, *Colloid Polym. Sci.* **1993**, *271*, 469.
[3] L. Onsager, *Ann. N.Y. Acad. Sci.* **1949**, *51*, 627.
[4] D. Frenkel, B. M. Mulder, *Mol. Phys.* **1985**, *55*, 1171. J. A. Veerman, D. Frenkel, *Phys. Rev. A* **1992**, *45*, 5632.
[5] J. U. Noeckel, A. D. Stone, *Nature* **1997**, *385*, 45.
[6] A. van Blaaderen, A. Vrij, *Langmuir* **1993**, *8*, 2921.
[7] K. P. Velikov, A. van Blaaderen, unpublished. Preliminary results published in: A. van Blaaderen, *MRS Bull.* **1998**, *23*, 39.
[8] E. Snoeks, A. Polman, C. A. Volkert, *Appl. Phys. Lett.* **1994**, *65*, 2487. E. Snoeks, T. Weber, A. Cacciato, A. Polman, *J. Appl. Phys.* **1995**, *78*, 4723.
[9] S. Klaumünzer, *Radiat. Eff.* **1989**, *110*, 79.
[10] A. Benyagoub, S. Löffler, M. Rammensee, S. Klaumünzer, *Nucl. Instrum. Methods Phys. Res.* **1992**, *B65*, 228.
[11] M. L. Brongersma, E. Snoeks, T. van Dillen, A. Polman, *J. Appl. Phys.* **2000**, *88*, 59.
[12] H. Trinkaus, A. L. Ryazanov, *Phys. Rev. Lett.* **1995**, *74*, 5072.
[13] M. L. Brongersma, E. Snoeks, A. Polman, *Appl. Phys. Lett.* **1997**, *71*, 1628.
[14] Here only the smaller particles (with 290 nm diameter) were used because the ion range of 500 keV Xe in silica is about 250 nm.
[15] N. Moriya, Y. Shacham-Diamand, R. Kalish, *Appl. Phys. Lett.* **1990**, *57*, 108.
[16] S. M. Scholz, R. Vacassy, J. Dutta, H. Hofmann, M. Akinc, *J. Appl. Phys.* **1998**, *83*, 7860. S. M. Scholz, R. Vacassy, L. Lemaire, J. Dutta, H. Hofmann, *Appl. Organometal. Chem.* **1998**, *12*, 327.
[17] A. van Blaaderen, *MRS Bull.* **1998**, *23*, 39.
[18] A. van Blaaderen, R. Ruel, P. Wiltzius, *Nature* **1997**, *385*, 321.
[19] J. W. Haus, H. S. Sözüer, R. J. Inguva, *J. Mod. Opt.* **1992**, *39*, 1991.
[20] F. M. van der Kooij, H. N. W. Lekkerkerker, *J. Phys. Chem. B* **1998**, *102*, 7829.

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