

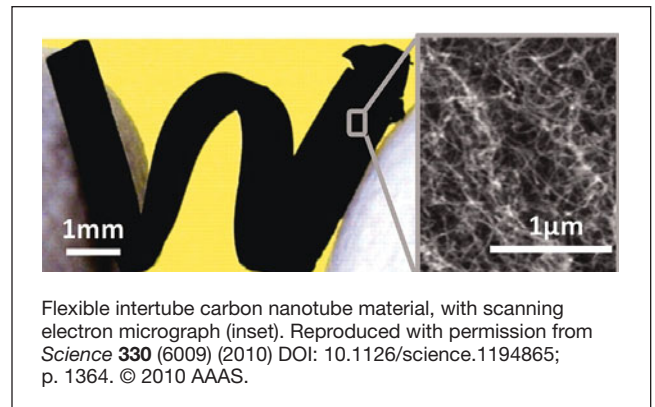
Nano Focus
Temperature-invariant viscoelasticity from -196°C to 1000°C achieved in CNTs

The physics of carbon nanotubes (CNTs) has rapidly evolved into a research field since their discovery by Iijima in 1991. Since then, theoretical and experimental studies in various fields such as electronics, biotechnology, optic, and mechanics have focused on both the fundamental physical properties and on their potential applications of CNTs. Recently, collaborative efforts of K. Hata and colleagues from the Technology Research Association for Single Wall Carbon Nanotubes (TASC), Nanotube Research Center, Institute of Advanced Industrial Science and Technology (AIST), and Japan Science and Technology Agency in Kawaguchi, Japan realized viscoelastic behavior in CNTs. The researchers assembled the material from a random network of long interconnected carbon nanotubes that exhibited an operational temperature ranging from -196°C to 1000°C .

As reported in the December 3rd, 2010 issue of *Science* (DOI: 10.1126/science.1194865; p. 6009), the researchers synthesized transverse long CNTs with a very high density of intermittent physical interconnections using a com-

bination of reactive ion etching, water-assisted chemical vapor deposition (CVD), and compression. These CNTs produced contained $\sim 68\%$ double-walled CNTs, $\sim 22\%$ single-walled CNTs, and $\sim 10\%$ triple-walled CNTs of 0.009 g/cm^3 , 4.5 mm in height and 99.9% carbon purity. The researchers observed an intertube structure where CNTs transverse laterally, making interconnections with other CNTs using a scanning electron microscope (SEM) (see Figure). The researchers observed a 100% strain from a shear-mode dynamic mechanical analysis (DMA) with high nonlinearity.

After further looking into the mechanism of viscoelasticity of these tubes, the group concluded that the strain was absorbed at low level by reversible unfolding of the traversing CNTs and 100% strain by an irreversible process of straightening, slipping, and bundling of CNTs. They also observed a closed hysteresis without abrupt changes which is typical for viscoelastic energy dissipative and highly deformable materials such as rubber. The CNT material synthesized had a similar stiffness (storage modulus



Flexible intertube carbon nanotube material, with scanning electron micrograph (inset). Reproduced with permission from *Science* **330** (6009) (2010) DOI: 10.1126/science.1194865; p. 1364. © 2010 AAAS.

$= 1\text{ MPa}$), high dissipation ability (loss modulus $= 0.3\text{ MPa}$), and damping ratio (0.3) than silicon rubber at room temperature. These viscoelastic properties were measured over a wide range of temperature from -196°C to 1000°C . Further analysis at this temperature range demonstrated temperature-invariant frequency stability, and the same level of reversible deformation and fatigue resistance.

The CNT material not only demonstrates thermal stability, but also provides temperature-invariant viscoelasticity and thus can be used as building blocks of thermally stable and viscoelastic materials in various applications, from human tissues, shoe soles, ear plugs, and mattresses to vibration isolators.

Jean L. Njoroge

 $\text{Er}^{3+}/\text{Pr}^{3+}$ co-doped fluorophosphate glass shows emission at $2.7\text{ }\mu\text{m}$ promising for solid-state laser development

The development of mid-infrared lasers operating in the infrared region around $2.7\text{ }\mu\text{m}$ is an active research field due to its applications including military and remote sensing, atmosphere pollution monitoring, eye-safe radars, and medical surgery. In the search of materials for the development of efficient optical devices based on rare-earth ions, two key factors are considered: glass host and the active ions. The glass host should have a high transparency in the mid-infrared

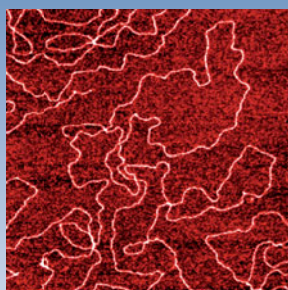
region and thus should have a minimal absorption in the typical OH^- absorption band at $3\text{ }\mu\text{m}$, low-nonradiative decay rates, high-radiative emission rates, and compatibility with fiber and waveguide fabrication processes. As the choice of ion for emission in the mid-infrared, Er^{3+} is well known for emission around $1.55\text{ }\mu\text{m}$ and $2.7\text{ }\mu\text{m}$. However, the $2.7\text{ }\mu\text{m}$ emission is usually not efficient unless co-doped with other rare-earth ions such as Pr^{3+} , Tm^{3+} , Yb^{3+} , Nd^{3+} , or Ho^{3+} .

In the January 15th issue of *Optics Letters* (DOI: 10.1364/OL.36.000109; p. 109), Y. Tian, R. Xu, L. Zang, L. Hu, and J. Zhang in a joint collaboration of the Chinese Academy of Sciences in Shanghai and Beijing report the obser-

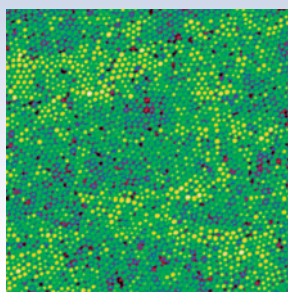
vation of $2.7\text{ }\mu\text{m}$ emission from diode pumped $\text{Er}^{3+}/\text{Pr}^{3+}$ co-doped fluorophosphate glass. They said that the good thermal properties and spectroscopic characteristics make this material promising for the development of a $2.7\text{ }\mu\text{m}$ laser.

The researchers have produced a fluorophosphate glass with the molar composition $20\text{Al}(\text{PO}_3)_3 \cdot 80\text{Rf}_2 \cdot 3\text{ErF}_3 \cdot 0.6\text{PrF}_3$ ($\text{R} = \text{Mg}, \text{Ca}, \text{Sr}, \text{Ba}$). The thermal analysis of the prepared glass reveals that ΔT defined as $T_x - T_g$, wherein T_x is the onset crystallization temperature and T_g is the glass transition temperature, is 238.7°C . This value is significantly higher than that reported for other fluorophosphates and fluoride glasses and indicates that the investigat-

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ed fluorophosphates glass composition possess a better thermal stability which can achieve a larger working range during optical fiber drawing. Investigation of the doped glass IR transmission spectrum shows that the transmittance of the glass in the infrared is as high as 90% and that the absorption around 3 μm , related to the OH^- absorption band, is negligible. Finally the infrared

photoluminescence studies show a strong 2.7 μm emission band for the codoped $\text{Er}^{3+}/\text{Pr}^{3+}$ glass, which is not present for the only Er-doped glass. Analysis of the upconversion spectra in the green visible range shows that this behavior is due to an energy transfer process in which the presence of Pr ions participate, and as a result the 1.55 μm Er emission is weakened while the 2.7 μm emission is

enhanced. Furthermore, peak of calculated emission cross-section in $\text{Er}^{3+}/\text{Pr}^{3+}$ doped fluorophosphates glass at 2708 nm achieves $(6.57 \pm 0.11) \times 10^{-21} \text{ cm}^2$ which is higher than the result of Er^{3+} doped oxyfluoride transparent glass ceramics ($4.3 \times 10^{-21} \text{ cm}^2$) and ZBLAN glass ($5.7 \times 10^{-21} \text{ cm}^2$).

Rosalía Serna

Nano Focus

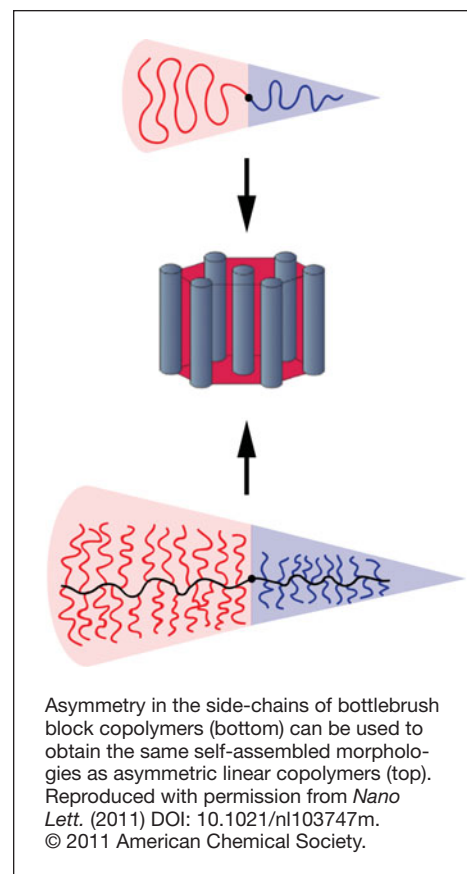
Bottlebrush copolymers expand size range of nanopores

The wide variety of nanostructured morphologies derived from the self-assembly of block copolymers provides a useful route to nanoporous materials. Degrading one of the polymer blocks leaves a porous network of the remaining polymer, which can be used for filtration and selective crystallization. Their main limitation is the small pore sizes currently accessible, but recent research by J. Rzayev and J. Bolton at the University at Buffalo and T.S. Bailey of Colorado State University shows that this range can be significantly extended by the use of so-called “bottlebrush” copolymers, in which polymer side-chains fan out from a central backbone.

The morphology of self-assembled block copolymer materials is normally controlled by altering the length ratio of the two blocks, giving rise to segregated regions in the form of flat planes, cylinders, or spheres. Bottlebrush copolymers, which can have polymer side-chains of different lengths, offer another variable with which to alter the space taken up by each block and thus the morphology they adopt. The research, published in

the January 31st online edition of *Nano Letters* (DOI: 10.1021/nl103747m), uses asymmetrical bottlebrush polymers consisting of a block with long polystyrene side-chains and one with shorter polyactide side-chains. Using a combination of controlled radical and ring-opening polymerizations, the team synthesized a methacrylate-based block copolymer and then grew the side-chains sequentially from this backbone. Melt pressing and annealing the polymer results in randomly oriented polyactide cylinder domains, which were aligned by channel die processing. Degrading the polyactide chains in alkaline conditions leaves a polystyrene material with nanoscale channels ($55 \pm 16 \text{ nm}$) running the width of the sample. This represents a substantial increase in size over pores derived from ordinary block copolymers (up to 35 nm), and it is likely that a much greater range is accessible by appropriate tailoring of the side-chains.

A potentially useful side effect of fabricating the material in this way is that the polymethacrylate backbone remains intact and present within the pores. The most striking consequence of this is that despite the material being principally polystyrene, the pores are hydrophilic and can uptake water. These leftover



backbones could also provide a useful scaffold for chemically modifying the pores in a host of ways.

Tobias Lockwood

Energy Focus

Light-trapping Si PVs obtained by UV-nanoimprint lithography

Light-trapping is necessary to achieve low-cost and high-efficiency thin-film Si photovoltaics devices. Many

nano-architectures leading to light scattering have greatly improved efficiencies although their ideal characteristics remain uncertain. C. Battaglia and co-workers from the École Polytechnique Fédérale de Lausanne recently used UV-nanoimprint lithography to fabricate

12% efficiency micromorph (a-Si:H/ $\mu\text{-Si:H}$) tandem cells with identically nanostructured ZnO and In_2O_3 :H front electrodes.

As described in the February 9th issue of *Nano Letters* (DOI: 10.1021/nl1037787; p. 661), the researchers used