

stable structure is nonmagnetic, has a volume per atom 5.2% larger than in diamond (in good agreement with experiment), and shows a slight elongation of the cubic cell along the (111) axis. The researchers found this configuration to be the most stable after considering all possible positions for two B atoms in a 12-atom supercell. The density of states at the Fermi level for BC_5 was found to be two times larger than for B-doped diamond with $\delta = 0.028$, showing that the number of carriers does not saturate even at $\delta = 0.167$. The average electron-phonon coupling for BC_5 is approximately 0.89, which is comparable to the coupling for MgB_2 . The researchers' analysis showed that the dominant contribution to the electron-phonon coupling comes from the vibrations of the B-C bonds. The researchers said that the large elastic constants in superhard materials require short, strong chemical bonds (typical of materials composed of light elements) that result in energetic phonons. Doping sufficient to sustain moderate electron-phonon coupling results in high- T_c superconductivity. Noting that the grain size of the BC_5 aggregates is only 10–15 nm and that bulk superconductivity is possible only if the coherence length is at least comparable to the size of the grains, Calandra and Mauri said that "it is necessary to grow larger samples, possibly by longer synthesis or by the use of catalysts to speed up the reaction."

STEVEN TROHALAKI

Spin-Polarized Excitonic Photoluminescence Observed in Mn^{2+} -Doped Colloidal CdSe Quantum Dots

Colloidal transition-metal-doped semiconductor nanocrystals have been attracting interest in spintronics, bioimaging, and other fields. However, an undesirable side effect of metal-ion doping is that it often leads to quenching of excitons by energy transfer to the dopants followed by nonradiative recombination. R. Beaulac of the University of Washington, X. Liu of the University of Notre Dame, S. Lee of Korea University, and their co-workers have now reported that the excitonic emission of Mn^{2+} -doped CdSe nanocrystals can be retained and co-exists with strong dopant-exciton magnetic exchange coupling by using quantum confinement to tune the CdSe excitonic levels to below all dopant excited states.

As reported in the March 2008 issue of *Nano Letters* (DOI: 10.1021/nl080195p; p. 1197), the researchers prepared a series of colloidal Mn^{2+} -doped CdSe nanocrystals with diameters in the range of $2 \text{ nm} < \delta < 5 \text{ nm}$ by using a soft chemistry synthesis

approach and measured their absorption and luminescence spectra. It was found that there are two luminescence peaks for small nanoparticles. The higher-energy peak coincides with the first exciton of the CdSe nanocrystals, whereas the lower-energy luminescence peak is attributed to the ${}^6\text{A}_1 \leftarrow {}^4\text{T}_1$ ligand-field transition of Mn^{2+} that is sensitized by CdSe quantum dot (QD) excitation. In contrast, the luminescence spectrum of the larger nanoparticles shows only one major peak, which corresponds to the excitonic emission of CdSe nanocrystals. The photoluminescence results also demonstrate that the energy of the excitonic transition depends on the particle size, but the energy of the Mn^{2+} transition does not. Nanocrystals at diameters of $\sim 3.3 \text{ nm}$ transition between the quenched and unquenched excitonic emission of CdSe nanocrystals.

The large Mn^{2+} -doped CdSe nanocrystals are unique because they show excitonic photoluminescence that is not quenched by the dopants, even though the excitons still interact strongly with the dopants. This was demonstrated using magneto-optical spectroscopies, which confirmed the existence of giant excitonic Zeeman splittings in the CdSe excitonic photoluminescence. In order to define the Zeeman splitting of the as-synthesized Mn^{2+} -doped CdSe nanocrystals, magnetic circular dichroism spectroscopy and magnetic circularly polarized luminescence spectroscopy were measured at low temperature as a function of applied magnetic field. Both techniques show the existence of giant excitonic Zeeman splittings in these diluted magnetic semiconductor (DMS) colloids comparable to those of the best molecular-beam-epitaxy-grown DMS QDs. These results demonstrate spin-polarizable excitonic photoluminescence in these colloidal quantum dots. These kinds of DMS nanocrystals are attractive because they are more processable and more easily handled than analogous materials grown by molecular-beam epitaxy. They therefore introduce new opportunities for studying and applying diluted magnetic semiconductors in nanotechnology including spin-electronic and spin-photon architectures, said the researchers.

ZHAOYONG SUN

Reductive Hydrothermal Synthesis of $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} Nanophosphors Yields Stronger Photoluminescence Compared with Normal Hydrothermal Method

Rare earth orthophosphates have been widely used as phosphors. Hydrothermal synthesis of rare earth orthophosphates, especially for $\text{LaPO}_4:\text{Ce}^{3+}$, Tb^{3+} (LAP), has

attracted attention due to its low temperature, high homogeneity, high purity, and simplicity. Ce is used as a sensitizer because of the efficient energy transfer between Ce^{3+} to Tb^{3+} . However, oxidation of Ce^{3+} to Ce^{4+} at the hydrothermal stage leads to the loss of luminescence. H. Zhu and co-workers at the Center of Materials Engineering, Zhejiang Sci-Tech University, China, have developed a reductive hydrothermal method by using hydrazine hydrate as a protecting agent, preventing the oxidation of Ce^{3+} to Ce^{4+} , to synthesize high-brightness LAP nanophosphors. The as-synthesized LAP nanophosphors exhibit a high-quenching concentration of Tb^{3+} and the $\text{La}_{0.4}\text{Ce}_{0.4}\text{Tb}_{0.2}\text{PO}_4$ nanophosphor shows almost the same PL intensity as that of the commercial $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder.

As reported in the May issue of the *Journal of the American Ceramic Society* (DOI: 10.1111/j.1551-2916.2008.02320.x; p. 1682), the researchers prepared a series of LAP nanophosphors by a normal and a reductive hydrothermal method and $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder by a coprecipitation method in order to identify the photoluminescent (PL) properties of LAP synthesized by different methods.

The structures and morphologies of the products were determined using x-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. All LAP samples synthesized show monoclinic structures and exhibit uniform nanorods 10 nm in diameter and 100 nm in length. The PL emission spectra of LAP nanophosphors synthesized by the reductive hydrothermal method show that the PL intensity of LAP nanophosphors increased with increasing Ce^{3+} and Tb^{3+} concentration. The quenching concentration of the LAP nanophosphors ($\sim 20\%$) is higher than that of its bulk powder. The PL intensity of one typical LAP nanophosphor $\text{La}_{0.85}\text{Ce}_{0.1}\text{Tb}_{0.05}\text{PO}_4$ synthesized by the reductive hydrothermal process is much higher than that of the same formula LAP synthesized by the normal hydrothermal process because the reductant prevented the oxidation of Ce^{3+} to Ce^{4+} , which can reduce the energy transfer between Ce^{3+} and Tb^{3+} . Moreover, $\text{La}_{0.4}\text{Ce}_{0.4}\text{Tb}_{0.2}\text{PO}_4$ shows a similar PL intensity as the $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ bulk powder. The researchers also conducted PL decay measurements of three $\text{La}_{0.7}\text{Ce}_{0.2}\text{Tb}_{0.1}\text{PO}_4$ products of bulk powder, nanophosphor prepared by the reductive hydrothermal method and by the normal hydrothermal method. The result shows that the PL lifetime of bulk powder is longer than that of nanophosphors. In addition, LAP nanophosphors prepared by the reductive

hydrothermal process exhibit longer lifetime than those prepared by the normal hydrothermal process. The researchers concluded that the reductive hydrothermal process is desirable for the synthesis of other efficient Ce³⁺- or Tb³⁺-doped nanophosphors.

ZHAOYONG SUN

A New Synthesis Route Yields Mg- and Zn-Doped GaN Powders with Blue-Violet Cathodoluminescence

Gallium nitride thin films on different substrates have been extensively produced and studied due to the direct wide bandgap semiconductor properties of GaN. H.-L. Li and collaborators of the National Institute for Materials Science in Tsukuba, Japan, obtained GaN powders, pure or doped with well controlled amounts of Mg or Zn by employing a high yield fabrication method involving the direct transformation of metal oxides into their nitrides under a flow of ammonia.

As the researchers reported in the May issue of the *Journal of the American Ceramic Society* (DOI: 10.1111/j.1551-2916.2008.02338.x; p. 1711), powders of GaN containing up to 2 at% Mg or Zn have been synthesized in a horizontal tube furnace heated under a flow of ammonia at 800–1000°C, and then cooled down to room temperature while keeping the ammonia flow constant. Subsequent x-ray powder diffraction, induction coupled plasma, and oxygen-nitrogen analyzer measurements revealed an almost perfect nitridization of the precursor Ga₂O₃ powder, coupled with a well controlled incorporation of Mg and Zn by stoichiometric addition of their corresponding oxides in the initial mix, while scanning electron microscopy imaging of the resulting powders showed a structure of compact

agglomerations of 100–200 nm crystallites.

Cathodoluminescence (CL) measurements revealed that the doped powders exhibit a bright blue-violet emission (at 3.05 eV for Mg, and 2.81 eV for Zn as the dopant), and offered evidence that the metals are incorporated as acceptors, a desired condition for optoelectronic applications. The CL intensity of the emission reached a peak for 1.0 at% of doping metals for both Mg and Zn. Longer time CL measurements demonstrated that the stability of the intensity increased with increasing Mg concentration, with a saturation also for 1.0 at%, where a loss of intensity of 36% was recorded after one hour, with respect to 60% loss for undoped samples. Further studies on the dependence of the CL intensity on the accelerating voltage and beam intensity showed a continuous increase with no brightness saturation in the range of 1.5–19 kV, and 400–2500 pA, respectively, which makes this type of material a good candidate for electroluminescent devices applications, said the researchers.

EUGEN PANAITESCU

Surface Plasmon Resonance and AFM Targeting Selectively Melts and Evaporates Gold Nanoparticles

E.A. Hawes and collaborators at the University of Kentucky have demonstrated an approach to selectively melt and evaporate gold nanoparticles that may soon be a low-energy approach to nanoscale patterning of different particles on substrates, as reported in the June 15 issue of *Optics Letters* (DOI: 10.1364/OL.33.001383; p. 1383).

Gold nanostructures (50 nm and 100 nm in diameter) exhibit enhanced optical absorption at wavelengths associated

with surface-plasmon resonance (SPR), where sharp, silicon atomic force microscopy (AFM)-probes enhance the electromagnetic fields near their tips. Earlier research referenced in the article showed that particle shape, size, and surrounding media play an important role in determining the energy absorption.

Spherical, gold nanoparticles were dispersed on a glass microscope slide and placed in contact with an equilateral BK7 glass prism using index matching fluid. Then 532-nm light from a 15 mW laser was reflected (on the side opposite of the sample) at an angle of incidence over 70° to achieve total internal reflection. The scan speed of the AFM probe (silicon tip, 10-nm radius, half-cone angle of 20–25°) determined the interaction time between the SPR energy field and the gold nanoparticles. The data shows that melting/evaporation only occurs in conjunction with the SPR-wavelength radiation and the close proximity of the AFM tip to the nanoparticles.

Two important demarcation points appear from the data: (i) a minimum interaction time with the probe, and (ii) a corresponding calculated minimum energy needed to melt/evaporate the particles. In addition to scan speed, the threshold interaction time is a function of particle size and distance between the probe tip and particle sample. It should be noted that multiple passes by the probe did not appear to have a cumulative effect as the radiative cooling of the nanoparticles happens in a relatively short time compared to the lapsed time between passes by the probe. The researchers said that near-field radiation transfer and detailed emission/absorption mechanisms continue to be explored.

THAD AWEKA

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