

# Rare-earth Information Center

# Insight

Ames Laboratory  
Institute for Physical Research and Technology  
Iowa State University, Ames, Iowa 50011-3020 U.S.A.

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## Rare Earth Pigments

Over the years, we have become accustomed to bright colors in a wide variety of materials. Cobalt blue is synonymous with the deepest blue ceramic glaze. Unfortunately, it seems that many of the pigments that give the strongest colors, are at best ecologically questionable. Thus, in the area of pigments, as in many other areas, there is an interest in highly stable nonreactive compounds containing rare-earth oxides. These pigments offer not only the chance of an environmentally benign color, but also, due to their stability, they are compatible with higher temperature processing so that they may be molded into plastics. Unfortunately, pure  $RE_2O_3$  pigments would lead to a rather subdued world, as they range from pure white to very weak pastel colors. B. Gonzalvo et al. {*J. Alloys Compds.*, **323-324**, 372-5 (2001)} have recently studied the  $(Bi,RE)_2O_3$  mixed oxides as possible pigments.  $\delta$ - $Bi_2O_3$  has been extensively studied because of its high oxygen ion conductivity. Unfortunately, this phase is stable over a relatively narrow temperature range from 730-825°C. Since a major application for high oxygen ion conductivity is in solid state fuel cells, there has been considerable interest in stabilizing the  $\delta$  phase at lower temperatures. This has successfully been achieved by partial substitution of the  $Bi^{3+}$  by  $RE^{3+}$  ions. The structure, which is a defective fluorite structure with  $\frac{1}{4}$  of the anion sites vacant, can be stabilized below room temperature. Gonzalvo et al. have studied substitutions of Nd, Sm and Dy in the  $\delta$ - $Bi_2O_3$  structure for pigment applications. For Sm  $x=0.4$  and Dy  $x=0.35$ , a single  $\delta$ -phase is obtained. The results for Nd,  $x=0.2$  and  $0.5$  are far more complex. Papers on color pigments and phosphors published in black and white journals are somewhat frustrating as one

is presented with color and reflection parameters, which are meaningless to those of us not well versed in the field, however, the authors report that the values of lightness and purity of color, and the reflectance percentage obtained for the Sm and Dy substitutions are suitable for use as pigments.

## Photoluminescence of $Eu^{3+}$ in $TiO_2$

As we have often discussed, the requirements for optoelectronic devices and flat panel displays drive much of the current research in photoluminescence materials. Compared to conventional CRT displays, the operating voltage of these displays is much lower, and consequently the currents must be higher. The high current densities appear to result in degradation of conventional phosphors over time. Rare-earth ions are attractive in phosphors, because the position of the luminescence lines is dependent on the electronic structure of the rare earth 4f shell and is largely independent of the host matrix. However, the relative intensity of the luminescence lines is dependent on the host, since various levels may be excited differently depending on such things as the host phonon spectrum. Useful phosphors face an additional requirement that their processing be compatible with the requirements for device fabrication. As a result, sol-gel processing of a large number of RE-host matrix combinations is currently under investigation. One such system is  $TiO_2(Eu^{3+})$ , which has been investigated by A. Conde-Gallardo et al. {*Appl. Phys. Lett.*, **78**, [22], 3436-8 (2001)}. Thin films were prepared on both glass and Si wafers by a standard sol-gel process. The films show an intense red photoluminescence associated with the  $Eu^{3+}$  transition with the peak energy position, spectral shape and width all independent of temperature over the 12-300 K temperature range, which makes the material attractive for technological applications.

## Rheology of Hot-forged NdFeB

In the May 2001 RIC *Insight*, I discussed a paper on sintering of Nd-Fe-B magnets. The goal in sintering of permanent magnets is to obtain a highly textured, extremely fine grained structure in order to obtain both high magnetization and coercivity. Metallurgical speaking, powder metallurgy is a relatively new process, and there are historically proven processes for producing fine grain size and texture. Hot-forging is one of the oldest known of these processes. I will refrain from quoting Longfellow's "The Village Blacksmith", but the process remains essentially the same, you heat up the metal and then hit it with a hammer. Of course, we now discuss such things in terms of dynamic deformation modes at high strain rates, but it still comes down to how hot, and how big the hammer is. The understanding of these processes is quite complex, and there are a number of grain refinement mechanisms, which can be active during hot deformation. S. Rivoirard et al. {*Mater. Sci. Eng. A*, 311, 121-7 (2001)} have designed a hammer for applying dynamic deformation modes at very high strain rates and applied it to Nd-Fe-B-Cu alloys. They have compared the results to those on the same alloys at much lower strain rates obtained in an Instron process. The samples are 20 g ingots cast into stainless steel tubes, which have endcaps welded on to prevent oxidation. The samples are induction heated and then a 150 kg metal hammer is dropped on the material with a maximum velocity of 4.7 m s<sup>-1</sup>. If I remember my high school physics, that corresponds to dropping the hammer about 2.2 meters. The strain rate depends on the geometry and rheology of the sample, but it is an order of magnitude greater than in the conventional press. Needless to say, stress strain curves were only recorded in the conventional press. Forging temperatures between 850 and 1400 K were used. The compositions used were such that there was liquid present in the samples during forging, and the liquid volume fraction increases linearly with increasing Nd content. The compositions were chosen for 0, 10 and 15%

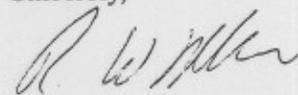
liquid volume fraction. As Nd<sub>2</sub>Fe<sub>14</sub>B undergoes a brittle to ductile transformation around 1273 K, the microstructure obtained is strongly dependent on the forging temperature. Brittle fracture of the grains resulted in higher coercivity for forging temperature below 1273. On the other hand, the induced fiber texture was enhanced when the deformation was in the ductile mode. The best values of BH<sub>max</sub> were 200 kJ m<sup>-3</sup> obtained for 10% liquid volume fraction at 1173 K.

## Short Notes

On September 27, 2001, Magnequench, Inc. announced the closure of its Anderson, Indiana production facility. The plant employs 200 hourly employees. The press release sites "a series of unforeseen economic circumstances, including the collapse of the technology sector" as the cause of the closure. The company notes that 90% of its customer base is in Asia and almost all of the raw materials for powder products come from China {[www.magnequench.com](http://www.magnequench.com)}.

The U.S. Department of Energy has selected four new government-industry projects as part of a \$500 million, 10-year effort to produce breakthrough solid state fuel cells that will eliminate current cost barriers preventing wide scale applications. The winners in a competition to begin developing ultra-low-cost fuel cells are proposals from Honeywell, Inc., Torrance, CA; Siemens Westinghouse Power Corp., Pittsburgh, PA; the team of Delphi Automotive Systems, Flint, MI, and Battelle, Columbus, OH; and the team of Cummins Power Generation, Minneapolis, MN, and McDermott Technology Inc., Alliance, OH. The Energy Department's goal is to cut the costs of fuel cells to as low as 1/10th the cost of currently marketed systems and to only 1/3rd the cost of the more advanced concepts now beginning to reach commercial readiness. The solid state electrolytes used in these fuel cells typically contain rare-earth oxides {<http://www.energy.gov/HQPress/releases01/augpr/pr01137.htm>}.

Sincerely,



R. W. McCallum  
Director of RIC