

# Rare-earth Information Center

# Insight

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## Undercooling of $\text{Nd}_2\text{Fe}_{14}\text{B}$ Levitated Melts

$\text{Nd}_2\text{Fe}_{14}\text{B}$  does not melt congruently but rather peritectically decomposes into Fe plus liquid. As a consequence, when a liquid at the 2-14-1 composition is cooled, Fe is precipitated from the homogeneous liquid starting at the liquidus temperature, and 2-14-1 does not solidify until the material is cooled below the peritectic temperature. If the cooling rate is not sufficiently slow to allow dissolution of the primary Fe, the resulting ingot contains four phases. In order to obtain a single-phase ingot, a prolonged anneal is required. Using rapid solidification techniques, it is possible to cool through the temperature region where Fe should be formed before significant nucleation and growth can take place. All liquids must be cooled slightly below their liquidus in order for them to crystallize. This is a result of the fact that the surface between the liquid and solid has a certain surface energy, so that until the energy of the solid state is less than the energy of the liquid state by the surface energy of the interface, the liquid can not solidify. The degree of undercooling necessary depends on many factors. For some pure metals, it is possible to undercool the melt by hundreds of degrees. The undercooling, which can be achieved in  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , is limited by the ease of nucleation of Fe that can form on impurities or crucible walls. Recently, significant undercoolings of  $\text{Nd}_2\text{Fe}_{14}\text{B}$  have been reported by Volkman et al. {*Appl. Phys. Lett.*, **80**, [11], 1915-7 (2002)}, using levitation induction melting of a 1 gm sample. For  $\text{Nd}_2\text{Fe}_{14}\text{B}$ , it is not simple to obtain undercoolings below the peritectic temperature due to the presence of  $\text{Nd}_2\text{O}_3$ , which promotes nucleation. However, the authors point out that in the presence of excess Nd,  $\text{Nd}_2\text{O}_3$  reacts with the Nd at high temperature to form NdO, which is a volatile oxide. Starting with a composition of  $\text{Nd}_{14}\text{Fe}_{79}\text{B}_7$ ,

the authors claim to have purified their  $\text{Nd}_2\text{Fe}_{14}\text{B}$  by heating the levitated sample to 1700 K in 1 to 10 mBar of He for about 1 minute. Using a two-color pyrometer to measure temperature, they observed that they could undercool by as much as 110 K. They compared the results of undercooling 60 and 110 K to the undercooling of 5 K, which they observed when levitation melting the sample in 1 bar He. As is to be expected, the 5 K undercooling produced a considerable amount of primary Fe while the undercoolings below the peritectic showed very little Fe.

## Calcium Doped Ceria as UV Filters

In recent years, there has been a growing concern with skin cancer caused by exposure to the sun's UV radiation. Thus, there is considerable interest in finding effective UV absorbers. There are a couple of interesting aspects to this application. First, there is a market requirement that the sunscreen not make the wearer appear unnaturally white, and second that the absorbing material not cause reaction either with the skin or the other ingredients in the sunscreen.  $\text{TiO}_2$  and  $\text{ZnO}$  are effective absorbers, but they have high indexes of refraction that give the white appearance. They also have a high photocatalytic activity, which can cause oxidation.  $\text{CeO}_2$  has the appropriate band gap for UV absorption and is transparent to visible light. It is however an excellent catalyst. Previously, I have reported on methods used to coat the  $\text{CeO}_2$  in order to reduce its catalytic activity. However, coating the  $\text{CeO}_2$  reduces its UV-shielding effect. An alternative method of reducing the catalytic activity of  $\text{CeO}_2$  is to dope the material with  $\text{Ca}^{2+}$ . M. Yamashita et al. {*J. Mater. Sci.*, **37**, 683-7 (2002)} have studied the preparation of 2-4 nm particles of coped  $\text{CeO}_2$  by solution chemistry at 40°C. The

authors were able to dope up to 20 mol% Ca into the  $\text{CeO}_2$ . Under the appropriate conditions, the authors were able to produce much finer particles of the doped  $\text{CeO}_2$  than the undoped material. This resulted in enhanced absorption characteristics and also higher transparency to visible light.

### Microwave-hydrothermal Preparation of $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ Powders

As I have discussed before,  $\text{CeO}_2$  plays an important role in automotive catalytic converters. An essential feature of such converters is that they heat up very rapidly in order to eliminate a startup transient, which will cause the total emissions to exceed the regulatory limits. Unfortunately, rapid heating usually corresponds to placing the converter close to the engine and an increase operating temperature for the converter. Under these conditions, there is a tendency for the fine  $\text{CeO}_2$  particles that are necessary for good catalytic activity to coarsen, degrading performance. Therefore, there is considerable interest in finding methods of stabilizing fine  $\text{CeO}_2$  particles at high temperatures. The addition of  $\text{Zr}^{4+}$  has been shown to improve both oxygen storage and thermal stability of  $\text{CeO}_2$ , however, these properties are highly dependent on the preparation method. Recently, H. S. Potdar et al. {*Mater. Chem. Phys.*, **74**, 306-12 (2002)} have reported the successful synthesis of high surface area  $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$  powders by the microwave-hydrothermal route. In the hydrothermal synthesis of ceramic powders, metal salts, oxides or hydroxides are used in solution or suspension in a fluid, frequently water, and heated and reacted at high temperature and pressure typically 300°C and 100 MPa. The pressure is generated in a closed reactor as the temperature greatly exceeds the normal boiling point of water. Under these conditions, single-phase sub-micron particles of ceramic materials may be formed well below the temperature required for solid-state synthesis or the temperature required to crystallize powders made by co-precipitation. In microwave-hydrothermal reactions, the reaction takes place at an even

lower temperature and correspondingly lower pressures. Because of the lower temperature of the reaction, very fine powders can be obtained. The rates and energy efficiency of microwave-hydrothermal reactions are reported to be much higher than conventional hydrothermal. Potdar et al. used zirconyl nitrate, cerous nitrate and potassium hydroxide reacted at 200°C and 1.4 MPa. The product of the MH process is made up of agglomeration of primary particles about 6-7 nm in size. The agglomerates are 2-8  $\mu\text{m}$  in size. A 99% yield is reported for the process, and the material is said to be stable to 1000°C. In looking up information on hydrothermal synthesis, I came across an interesting article by D. Segal {*J. Mater. Chem.*, **7**, [8], 1297-305 (1997)} that outlines various synthesis routes for ceramic materials.

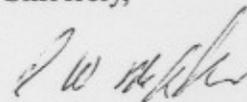
### Switchable Mirrors

Over the last several years, we have been following the progress in the production of mirrors that may be switched for transparent to reflecting by changing the H content of a  $\text{REH}_x$  thin film. T. F. Rosenbaum and A. F. T. Hoekstra {*Adv. Mater.*, **14**, [3], 247-50 (2002)} presented a brief overview of the progress that has been made toward a marketable device using this effect. In addition, they report a rather interesting phenomena. If a film in the insulating state is irradiated with UV at temperatures below 10 K, photoconductivity is induced. The strange part is that while photoconductivity can only be induced below 10 K, once induced the charge carriers persist for long times and survive at temperature approaching room temperature. This phenomena does not appear to be understood at this time.

### Company Notes

Vacuumschmelze has announced that it has produced  $\text{Nd}_2\text{Fe}_{14}\text{B}$  permanent magnets with an energy product at 20°C of 56.7 MGOe. The magnets were produced using laboratory facilities and have a remanent magnetization of 1.519 T with  $H_c$  of 9.9 kOe.

Sincerely,



R. W. McCallum  
Director of RIC