

# RARE-EARTH INFORMATION CENTER NEWS



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## Rare Earths In the News

### FERRIMAGNETS

Ferrimagnets, the odd magnetic materials widely used in radar circuits and computers, may find new applications as microwave signal amplifiers. Experiments at the Lockheed Research Laboratory in Palo Alto, Calif., have shown that resonance echoes in yttrium iron garnet ferrimagnets can amplify microwave signals by 50 db.

### SOLID ELECTROLYTES

Tubes of a thoria: yttria composition, acting as solid electrolytes or high temperature semiconductors, are used in high temperature fuel cells and as e.m.f. cells for measuring oxygen solubility in molten materials. The tubes were developed by Micropure, Ltd. of London.

### SUPERALLOYS

Yttrium, gadolinium, and thorium, which markedly improve surface stability of nickel superalloys, seriously degrade mechanical properties of cast alloys and narrow the hot working range of wrought alloys, according to studies by General Electric.

A vanadium alloy (V-20-Mo-10Ti) containing 0.5% yttrium has a tensile strength of 175,000 psi at room temperature and 21,000 psi at 1200°C, and at 815°C has a strength/density ratio superior to that of some well-known superalloys, reports the U.S. Bureau of Mines, Reno, Nev.

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## Rare Earths in Lunar Samples

The relative abundances of the rare earths in lunar samples may provide clues to unravel the complex chemistry of the moon. The results of the investigation of the 22 kg of lunar samples collected by Apollo 11 were presented at the Lunar Science Conference Jan. 5-8 and published in a special Jan. 30 issue of *Science*.

In general the distribution of rare earths in the lunar material resembles terrestrial oceanic andesite, Ca-rich achondrite, or abyssal basalt with the striking exception that the Eu content is about 60% lower relative to Sm and Gd. This Eu depletion could have been produced by  
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## Rare Earths Aid Pollution Fight

An application using Nd lasers to help solve air pollution problems has recently been developed by Culkowski, Swisher and Gifford of the Atomic Energy Commission's Oak Ridge National Laboratory. The system consists of a pulsed laser and associated optical and detector equipment, known as LIDAR for Light Detection and Ranging.

When LIDAR in conjunction with a telescopic system is aimed at a nearly invisible source of pollution, such as chimney effluents, the dispersion or behavior of particles in the effluent is revealed by means of projection and reflection of high intensity beams of light.

## Van Vleck Retires

Harvard University Professor John H. Van Vleck has retired from full-time teaching and research and is now Hollis Professor of Mathematics, Emeritus. He is well-known in the scientific community for his studies on magnetism and quantum theory of atomic structure.



Van Vleck

To us (the rare-earth community) he is the "father of rare-earth magnetism" for his contributions to the scientific foundation of the theory of the magnetic properties of the rare-earths. He was the keynote speaker at Fourth Rare-Earth Research Conference, Phoenix, April, 1964.

Among his many honors, Van Vleck was president of American Physical Society in 1952, and he has received the Langmuir Prize (American Physical Society), the Michelson Award (Case Institute of Technology), and the National Medal of Science.

## RE Products Make Top 100

The continuing progress of rare-earth technology was well represented when Industrial Research, Inc. named what it considered the 100 outstanding products of the past year's technical efforts. The IR 100, now seven years old, listed three products for 1969 employing rare earths.

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## ACS Award to Banks

Dr. Charles V.

Banks, professor of chemistry at Iowa State University, has won the 1970 American Chemical Society (ACS)



Banks

Award in Analytical Chemistry. Dr. Banks is also chemistry section chief at the Atomic Energy Commission's Ames Laboratory, Ames, Iowa.

The \$2,000 award, sponsored by Fisher Scientific Company, was presented to Banks at the ACS Spring Meeting in Houston on February 23.

Banks was nominated primarily for his over-all contributions to the science of analytical chemistry, including rare-earth materials.

## YTTRIUM

*Yttrium-Properties, Phase Diagrams, Industrial Applications* by V. F. Terekhova and E. M. Savitskii is now available as an English translation, 167 pages.

The authors have attempted to generalize the available literature data on the preparation and properties of yttrium, and the phase diagrams and properties of its alloys. The technological and mechanical properties as well as the physical, chemical, magnetic and electrical properties are discussed along with such topics as recrystallization, metallography, and single crystals. Almost all of the available binary and ternary phase diagrams are presented in the alloy section.

Although the authors believe that yttrium has not been studied on a sufficiently wide scale, the limited research has developed uses in the fields of metallurgy, nuclear energy, refractory materials, and medicine which are surveyed in the last section.

The translation, which includes 280 references, is available for \$3.00 from the Clearinghouse for Federal and Scientific Technical Information, Springfield, Virginia 22151, U.S.A.

## Rare-Earth Polymer

A rare-earth polymer ( $MG_3$ ) has been prepared by extracting the metallic ions from RE chloride or nitrate solutions with di(2-ethylhexyl)phosphoric acid (G).

T. Harada, M. Smutz, and R. G. Bautista of Ames Laboratory, Iowa State University, measured the physical and chemical properties of this polymer in which  $M=Y, Yb, Dy, Ho, Sm, Nd,$  and La. Molecular weight determinations for the yttrium polymer show the formula to be  $(YG_3)_{6000}$ .

*To our knowledge this is the first report of a rare-earth polymer.*

## RE Mineral Specimens

The Hoyt company has made available an 18-specimen case of rare-earth and reactive metal minerals for \$27.50. Purchasers have a choice of 18 of 27 rare-earth and reactive metal minerals. For more information write to: Hoyt, Mineral Specimens Division, 3049 N. Marigold Drive, Phoenix, Arizona 85018, U.S.A.

## RE Enrichment

The effect of geological environment on the composition of the rare earths in minerals has been illustrated by data on monazite, sphene, and apatite, compiled by M. Fleischer and Z. S. Altschuler in *Geochim. Cosmochim. Acta* 33, 725 (1969).

Alkalic and mafic rocks have been shown to be enriched by the light lanthanides in igneous processes, while the same process enriches granitic rocks, especially pegmatites, with the heavy rare earths. The effects of geological environment were found to be greater for minerals in which the rare earths appeared as minor constituents.

It was suggested that the geological source of monazite from various types of rocks could be determined by the average composition of the rare earths.

## IR Radiation To Visible Light

Several papers by L. G. Van Uitert, L. F. Johnson and their co-workers have described the materials, their preparation and mechanisms for converting infrared radiation to visible light. These papers appeared in *Appl. Phys. Letters*, 15, 48-50, 51-52, and 53-54 (1969) and *Mater. Res. Bull.* 4, 381-390 (1969).

In general the infrared radiation from a Si-doped GaAs diode ( $0.93\mu$ ) is converted to visible light by a rare-earth oxyhalide phosphor. The rare-earth oxyhalide contains Yb which absorbs infrared radiation and then transfers the energy to another lanthanide ion (generally Ho, Er or Tm) which emits visible radiation. A  $BaRF_5$  compound where R is Y or Lu can also be used as the host material instead of  $Y_3OCl_7$ . The  $Yb^{+3}, Er^{+3}$ -doped  $BaRF_5$  yields a green light, while the  $Yb^{+3}, Er^{+3}$ -doped  $Y_3OCl_7$  emits a red light.

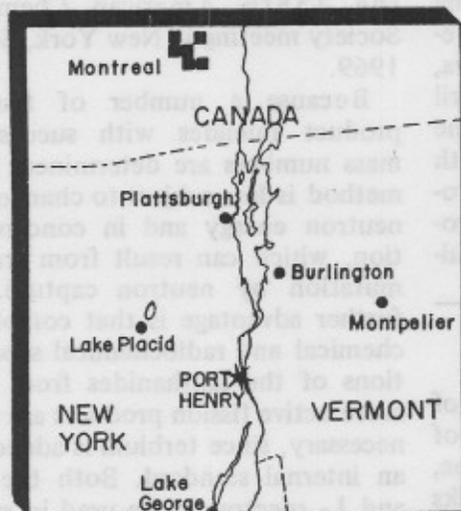
The authors furthermore point out that a "tunable" color can be obtained for certain Er-activated  $Y_3OCl_7$  phosphors by varying the GaAs diode excitation output. Color variations can also be obtained by varying the Yb concentration and/or by varying the lanthanide activator ion.

RE Products Make Top 100  
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One of these products was a samarium-cobalt permanent magnet, which has twice the strength of any conventional permanent-magnet material. Also in the list was a YIG-tuned "Gunn Effect" oscillator, used for microwave sweepers, analyzers, and broadband microwave receiver local oscillators. The third rare-earth development was an yttrium aluminum garnet laser utilizing a neodymium doped YAG rod. The laser, primarily for cutting and welding materials such as aluminum and silicon, can be frequency-doubled for high power uses.

## Iron RE Source

Rare earth-containing mineral piles at Republic Steel's Port Henry, NY, iron ore mine may be purchased by Molybdenum Corp. of America.



The apatite constituting 10% of the tailings includes the heavy rare earths yttrium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, europium, and gadolinium.

Molycorp's final decision to exercise its option and begin recovery and processing will depend partially upon further market development for these rare earths.

Rare Earths in the News  
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### TENNIS ANYONE?

British producer Magnesium Elektron (MEL) is making paddle tennis rackets from a 1% rare earth-magnesium alloy. MEL hopes to capture one-third of the market within three years by selling the rackets—which offer durability, attractiveness, and light-weight, flexible design—for about \$20.

### LIQUID SCINTILLATOR

Mineral-oil based gadolinium-loaded neutron scintillation detectors with efficiencies of 80% have been prepared at the Ames Laboratory. A gadolinium-2-ethylhexanoate and tri-n-octylphosphine oxide complex which is soluble in mineral oil is more stable and can be prepared more safely.

## RE-Doped Compounds

World-wide interest on the optical properties of another class of rare-earth doped materials is evident in several recent publications.

In Japan H. Komiya (*J. Phys. Soc. Japan*, 27, 893-901 1969) writes about the optical spectra of  $Tm^{+3}$ ,  $Li^+$  and  $Tm^{+3}$ ,  $Cu^+$ -doped ZnSe. He describes the crystal field effects and presents a model to account for the observed spectra.

The luminescent properties of lanthanide-activated CdS, with Cu as a co-dopant, is described by English investigators (Apperson, Garlick, Lamb and Lunn) in *Phys. Stat. Solidi*, 34, 537-544 (1969). Of the 11 lanthanides studied, seven exhibit line emissions. In these materials the luminescence is due to the lanthanide ion, which receives the energy absorbed at a Cu site via resonance transfer.

The electroluminescence of ZnS thin films containing lanthanide metal fluorides is discussed by American scientists (Chase, Heppelwhite, Krupka and Kahng) in *J. Appl. Phys.* 40, 2512-2519 (1969). They found that of the 12 fluorides investigated the ZnS/TbF<sub>3</sub> device had the brightest illumination, more than 50 ft-lamberts. Spectra for the 12 devices and energy level schemes were also given.

## L A S E R

The optical properties of Nd-doped crystalline and glass laser materials have recently been studied at 25°-200°C in an attempt to further the development of laser materials, *Applied Optics* 8, 1087-1102 (1969). In the first portion of their article, Thornton, Fountain, Flint and Crow made an extensive survey of the existing information on Nd-laser materials.

In the latter portion they described some of the more promising YAG and glass hosts. YAG-Nd was found to be more appropriate for high repetition rate Q-switched applications, although glass-Nd would also be good, if the optical

## Two More RIC Grants

Santoku Kinzoku Kogyo Co. Ltd. of Kobe, Japan, and Ban Eng Hong Tin Mining Co. Sdn. Bhd., of Ipoh, Malaysia, have joined the ranks of private industrial firms which provide financial assistance to RIC. The Center now receives support from 19 leading rare-earth companies from eight countries throughout the world.

distortion and birefringence caused by thermal effects could be improved. Further results showed that  $Cr^{+3}$ , as a sensitizer, enhanced the 1.06 $\mu$  fluorescence of YAG by as much as 20% 120 $\mu$  sec after initiation of the pump pulse.

Recent plasma research employing Nd-doped lasers was reported in *Physics Today* 22, 55 (Nov. 1969). High-temperature plasmas are being produced by Nd-doped glass laser systems which produce hundreds of joules in pulses lasting nanoseconds to picoseconds. University of Rochester scientists have produced 10<sup>4</sup> to 10<sup>6</sup> neutrons/pulse by focusing the laser on a solid droplet of deuterium.

At Lawrence Radiation Laboratory a tilted-disc laser amplifier system which contains 15 Nd-doped glass discs is expected to produce 1000 joules with a 50 cm<sup>2</sup> cross section for a few nanoseconds. The laser will be used to investigate high temperature (1-10keV) plasmas and sharp x-ray lines produced by focusing the laser output on a high-atomic number target.

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## Liquid Lanthanum

The structure factor of liquid lanthanum has been measured by neutron diffraction by M. Breuil and G. Tourand, *Phys. Letters* 29A, 506-507 (1969). They noted that the structure factor is significantly different from that of other metals. Two unusual features are the absence of oscillations in the intensity vs  $k$  (the distance in reciprocal space) plot below the critical  $k$  value, and the anomalous low intensity value for the strongest peak at a temperature close to the melting point.

The radial distribution function shows that there are 11 nearest neighbors at a distance of 3.75 Å. These values are essentially the same as in the solid.

*As far as we are aware this is the first determination of the radial distribution and structure factor for a liquid rare-earth metal. Results on other rare-earth metals would be of interest too, to see if they are similar to or different from lanthanum.*

## RE Chromites

The unique properties of the rare-earth chromites may lead to their use as electrode materials for magnetohydrodynamic (MHD) power generation. The chromites are not only refractory materials with melting points between 2310°C and 2490°C but also very good p-type electrical conductors, especially when doped with aliovalent impurities.

The ceramic and electrical properties of lanthanum chromite can be improved by doping with strontium carbonate according to D. B. Meadowcroft, *J. Phys. D.* 2, 1225-1233 (1969). The maximum density, hardness, strength, and thermal shock resistance were achieved by adding up to 4 mol% SrCO<sub>3</sub> to La<sub>0.84</sub>Sr<sub>0.16</sub>CrO<sub>3</sub> before final fabrication and firing in a reducing atmosphere at over 2030°C. The doped product has an electrical resistivity less than 10<sup>-2</sup> ohm m above room temperature, a

thermal conductivity of 5.1 w m<sup>-1</sup> degK<sup>-1</sup> between 830° and 1730°C, a thermal expansion coefficient of 9.0x10<sup>-6</sup> deg<sup>-1</sup> between 25°C and 830°C, and also excellent corrosion resistance.

The chromites of the rare-earth elements except Ce can be prepared by calcining the corresponding nitrates at 1000-1100°C as reported by Portnoy and Timofeyeva, English trans., AD-694,792 (April 1969). The melting point of the chromites decreases linearly with atomic number. All of the chromites were more resistant to corrosion than the corresponding sesquioxides.

### Rare Earth in Lunar Samples (Continued from Page 1)

partial melting (less than 20%) of the lunar mantle composed of feldspar, olivene, orthopyroxene, and opaque oxides; the lunar rocks would then represent liquids from different stages of this equilibrium melting. The relatively high abundance of the rare earths on the moon lends strength to another interesting speculation—that the lunar material is a condensate of solar nebula formed at temperatures which lie between the condensation temperatures of iron and nickel on the one hand and of sulfides and proton-rich materials on the other.

## Burnup Monitor

The determination of La, Ce, Pr, and Nd fission products by an x-ray spectrometric method was reported to be a new and accurate means of monitoring fast reactor oxide fuel performance by Dr. R. P. Larsen at the 158th American Chemical Society meeting in New York, Sept. 1969.

Because a number of fission product nuclides with successive mass numbers are determined, this method is less subject to changes in neutron energy and in concentration, which can result from transmutation by neutron capture. A further advantage is that complete chemical and radiochemical separations of the lanthanides from the more active fission products are not necessary, since terbium is added as an internal standard. Both the K- and L- spectra can be used in rare-earth x-ray spectroscopy.

## CONFERENCE REPORT

The February 1970 issue of *Physics Today* contains a summary of papers presented at the 1969 International Conference on Luminescence held at the University of Delaware Aug. 25-29. A number of papers, which may be of interest to some of our readers, are reviewed on pages 91 and 93 of this issue.

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