



RARE-EARTH INFORMATION CENTER NEWS

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INFRARED TO VISIBLE

The development and potential applications of anti-Stokes phosphors utilizing rare earth doped crystalline materials have been reviewed by G. F. J. Garlick [*Contemp. Phys.* 17 [2], 127-44 (1976)]. A relatively nontechnical description of quantum mechanics and solid state physics as related to anti-Stokes phosphors provides an interesting and informative background for even the nonspecialist.

Known as up-converters, anti-Stokes phosphors absorb infrared photons and combine their energies in multiples of twos or threes to emit new photons of increased frequency (decreased wavelength). Thus, infrared radiation absorbed by an anti-Stokes phosphor will produce radiation in the visible or ultraviolet region. Such a process would be useful for providing visual displays of infrared signals and images and would constitute a distinct advantage over conventional light emitting diodes for large area displays.

The rare earth ions Ho^{3+} , Er^{3+} , Tm^{3+} and Yb^{3+} are particularly useful as up-converters due to the well shielded electrons in the incompletely filled 4f shell. Yb^{3+} , a strong absorber of infrared radiation, functions as a sensitizer, transferring the absorbed energy to the other rare earth ions which are called activators. The efficiency of conversion is affected by (1) the amount of back transfer of energy from the activator to the sensitizer, (2) the characteristics of the crystalline host material, (3) the temperature, and (4) the presence of trace impurities in the matrix. The largest efficiencies (25-30%) have been reported for holmium-ytterbium doped hexagonal yttrium oxysulfide ($\text{Y}_2\text{O}_3\text{-Ho-Yb}$) at liquid

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3 RE in IR-100

Industrial uses of rare earths continue to expand and this year three rare earth products are listed in Industrial Research's IR-100 winners [*Industrial Research* 18, [10] (Oct. 1976)]. The IR-100 represent the top 100 products of 1976 as rated by Industrial Research. Brief descriptions of this year's rare earth products are given below.

Lanthanum beryllate single crystals doped with Nd are a new laser ion-host system which has high energy storage, high efficiency and polarized output. Advantages over YAG:Nd include five times the crystal growth rate, 100% increase in maximum length and diameter, 50% better optical damage resistance, two to three times the Q-switched energy storage, better energy conversion efficiency and linearly polarized output. This new laser system may find use in satellite networks and large-disc amplifiers in high energy applications besides pulsed Q-switched and low power cw laser applications.

Another laser device, this one using an yttrium lithium fluoride crystal doped with Ho, has earned recognition as a pulsed or continuous source of two micron laser radiation. This device features a closed cycle liquid nitrogen cooling system, Q switch range of 0 to 5 kHz, cw output of 5 W, peak power output of 25 kW at 50 Hz, and pulse width at 100 Hz at 100×10^{-9} sec.

An oxygen potential probe containing a thoria-yttria mixture has been developed to nondestructively measure the thermodynamic potential, and therefore the composition, of both irradiated and unirradiated nuclear fuel materials. It is designed to be used at 700 to 800°C in highly pure inert flowing gas. Another ap-

The Writing on the Film

Recent interest in the thermomagnetic writing on amorphous magnetic films has led Y. Mimura and N. Imamura to study the magnetic properties of amorphous Tb-Fe thin films [*Appl. Phys. Letters* 28, 746-8 (1976)] and amorphous Dy-Fe thin films [*Japan J. Appl. Phys.* 15, 937-8 (1976)]. Both of these materials exhibited a low Curie temperature (120°C and 70°C, respectively) and a large coercivity with sufficient perpendicular anisotropy to sustain magnetization normal to the film plane. These characteristics qualify these materials for application as magneto-optical storage mediums using Curie point writing [*Japan J. Appl. Phys.* 15, 933-4 (1976)]. The advantage the Dy-Fe and Tb-Fe films offer over amorphous Gd-Co films results from their lower Curie temperatures. In the Gd-Co films the thermomagnetic writing must be done using the compensation point which varies with film composition because the Curie point is too high. The Curie temperature varies only slightly with composition and thus makes the Dy-Fe and Tb-Fe films attractive alternatives for magneto-optical storage.

MOLYCORN Control of KBI

About 1.6 million shares, or 52% of Kawecki Berylco Industries (KBI) common stock has been purchased by Molycorp. This came in response to an offer by Molycorp in August to purchase 1 million shares of KBI common stock.

plication would be to measure compositional variations in other variable stoichiometry oxide ceramic bodies.

Electrochemistry

Graduate students and research scientists in the field of electrochemistry, analytical, physical, organic and inorganic chemistry, chemical engineering or corrosion science of the rare earths should be interested in the *Encyclopedia of Electrochemistry of the Elements*, Vol. 6, A. J. Rard, ed., Marcel Dekker, Inc., New York (1976). Chapter two, Scandium, Yttrium and the Lanthanides by H. B. Herman and J. R. Rairden, represents a comprehensive compilation and critical review of the descriptive electrochemistry of the rare earth elements. Much of the data are presented in tabular form. Topics covered include the standard and formal potentials in aqueous and nonaqueous solutions, and fused salts, equilibrium data, polarographic characteristics, kinetic parameters and double layer characteristics of cerium, europium and lanthanum, electrochemical studies and applied electrochemistry including electrowinning, electrorefining, corrosion and coulometric titration. The cost of this 341 page volume individually is \$64.00 and through subscription \$54.00.

Superconductivity Use

Superconductivity as a probe of the magnetic state of local moments in metals is reviewed by M. B. Maple [*Appl. Phys.* **9**, 179-204 (1976)]. Exemplary matrix-impurity systems, most of which contain rare earths either in the matrix and/or as the impurity, are examined. No attempt is made to be comprehensive in coverage. Three types of magnetic behavior of the impurity are distinguished and it is shown that they can be identified by the detailed behavior of the depressions of the superconducting transition temperature (T_c) as a function of the impurity concentration and the specific heat jump at T_c as a function of T_c . Maple maintains that the systematics of superconductivity in the presence of local moments are satisfactorily established enough to be able to "1) ascertain whether the solute spin is long-lived (magnetic) or short-lived (nonmagnetic) compared to thermal fluctuation lifetimes at superconducting temperatures, 2) determine the sign and magnitude of the conduction electron-impurity

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LaAl₂ Dislocations Damped

Large Bordoni-type peaks in the ultrasonic attenuation of LaAl₂ and LaAl₂ doped with gadolinium have been observed by G. Herrmann and H. E. Bommel [*Appl. Phys.* **10**, 81-4, (1976)]. These peaks result from energy dissipation from sound waves to the lattice through dislocations which lie nearly or exactly parallel to close-packed directions in the crystal lattice. There is only one peak in each sample and the peaks are so narrow that they can be described by the original Seeger model with only one activation energy and one frequency. These observations shed some light on several properties which were believed to be characteristic of Bordoni peaks. All the materials previously investigated had much broader experimental than theoretical peaks which is not the case with LaAl₂. There are no satellite peaks for LaAl₂ as in other materials (the Seeger model contains only one peak). The belief that the peak height is reduced by impurities is not supported here. Several other characteristics were confirmed qualitatively. The authors note that more systematic experiments need to be done and recommend LaAl₂ as an excellent candidate due to the ease with which comparisons can be made between experimental data and theoretical calculations.

Infrared to Visible

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nitrogen temperatures. However, conversion efficiencies are commonly 1 to 2 percent at ordinary temperatures and approach those of light emitting diodes only for the middle of the visible spectrum. Increased efficiency has been reported by replacement of the crystalline matrix with vitroc ceramic host materials. Another possibility is the use of Tm³⁺ as activator because this ion involves no back transfer with each jump up the energy ladder. However, solid solubility limits of thulium in host materials used thus far do not permit sufficient concentration of this rare earth ion.

Anti-Stokes phosphors for conversion of infrared radiation to the near infrared and for conversion of visible light to ultraviolet radiation are also being investigated by the author.

GMELIN HANDBOOK

Another volume of *System 39, Rare Earth Elements*, of the Gmelin Institute's *Handbuch der Anorganischen Chemie* has been published. *Part B1, History, Position in the Periodic System and Separation of the Raw Materials* is 184 pages long and costs \$138.20. An English translation of the table of contents, the forward, and marginal footnotes is included as in previous volumes. In addition, chapter 3 is written entirely in English.

Topics covered in the four chapters include (1) the history of the discovery of promethium, (2) atomic weight and isotopic abundances of the rare earths, (3) comparison of properties of atoms and ions along the lanthanide series, and (4) laboratory and industrial separation of the rare earths from raw materials. Chapter 4 comprises the main portion of this book (69%).

Applauds RE X-ray Screens

In a letter to the editor of the *New Zealand Medical Journal*, R. R. McFarlane expressed great admiration for new X-ray screens containing gadolinium and lanthanum [82 [551], 321 (1975)]. McFarlane's appraisal of the latest development in radiology when compared to currently used screens was as sunlight is to moonlight and described the experience as "being as near to that of Roentgen peering at his glowing platinocyanide crystals as we can hope to attain".

The author also noted that there are now rare earth screens available which reduce X-ray exposure by ~87% which is of great value for X-rays taken during pregnancy and for infants and children.

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Achievement Award

Achievement Award presented by the Industrial Research Institute. The award, an original work of art symbolizing creativity in industrial research, cited Van Uitert for developing and investigating many new materials, including electronic and magnetic crystals, phosphors, lasers, rare earth garnets and borosilicate glass for optical fibers. Dr. Van Uitert has been with Bell Laboratories since 1952 and is currently supervisor of the Solid State Materials Synthesis Group.

L. G. Van Uitert

Gd PUMPS HEAT

G. V. Brown has examined the possibility of a practical magnetic heat pump at or near room temperature [*J. Appl. Phys.* **47**, 3673-80 (1976)]. Gadolinium metal was used in these experiments because its Curie temperature (20°C) is in or near the desired operating temperature range of the heat pump. Under adiabatic conditions the application of a 7 Tesla (70 kOe) magnetic field to Gd at the Curie point resulted in a temperature rise of 14°C while applying the same field under isothermal conditions caused a heat release of 4 kJ/kg. Various temperature-entropy diagrams are discussed with respect to thermal cycles which could best utilize the area between the entropy-temperature plane. A thermodynamic regeneration technique is proposed to remove the load of the lattice and electronic heat capacities from the magnetic cycle. The efficiency of this type of cycle would approach the ideal Carnot efficiency. Ferromagnetic rare earth intermetallic compounds which might find application in such a system are also listed.

NEW MANAGER

Indian Rare Earths, Ltd. has named Mr. N. D. Hansotia as Acting Managing Director effective as of April 2 of this year following the resignation of Mr. P. Muralidharan from the services of the company.

Boyd and CeAl₃ [*Phys. Rev. Letters* **36**, 1332-5 (1976)].

The square of the effective moment of Ce can be reduced by either crystal field effects, a small spin correlation time, a compensating conduction electron polarization or a small value of the fractional occupancy of the localized 4f¹ configuration. The authors observed no evidence of a compensating conduction electron polarization in either system. Taking into account the remaining variables the fractional occupancy of the localized 4f¹ configuration at 11 K was calculated to be 0.9 to 1.0 for CeAl₃ and 0.4 ± .1 for Ce_{0.8}Th_{0.2}. Based on these results the Ce-Th alloy is clearly a configuration-fluctuation system and CeAl₃ is a possible candidate.

RARE EARTH VOLUMES

Volumes 25 and 26 of *Structure and Bonding*, edited by J. D. Dunitz, P. Hemmerich, R. H. Holm, J. A. Ibers, C. K. Jørgensen, J. B. Neilands, D. Reinen and R. J. P. Williams and published by Springer-Verlag, Heidelberg (1976), contain several articles which deal with the rare earths. Volume 25 consists of three rare earth articles, is 154 pages long and costs \$30.40. Volume 26 is devoted to spectra and chemical interactions but does contain one article on the rare earths. This volume is 144 pages long and costs \$23.80.

The narrow band thermoluminescence (candoluminescence) of rare earths in Auer mantles is reviewed by C. K. Jørgensen (Vol. 25). A brief history and theory are presented. Various compounds and ThO₂ doped with individual and different combinations of rare earths are discussed with respect to the thermoluminescence produced in the oxide mantles. The possible use of rare earth-containing mantles to burn hydrogen for illumination in a hydrogen economy is also included in the discussion (64 ref.).

E. C. Baker, G. W. Halstead and K. N. Raymond review the structure and

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Stone Award

recognition of outstanding service to the chemical profession, service which is not restricted to any particular branch or aspect of the profession. Boyd, currently a Professor of Chemistry at the University of Georgia, was one of the first chemists to join the Manhattan Project in 1942. He made some important contributions to the development of ion-exchange chromatography and its application to the separation of plutonium from uranium and its fission products, which include the rare earths. Before moving to Georgia he was associated with the Oak Ridge National Laboratory. He has served on the editorial boards of several scientific journals, participated widely in international conferences, and has been active in both the American Chemical and American Nuclear Societies.

G. E. Boyd

CONTRIBUTORS

Twelve more companies have contributed to the support of RIC during the second quarter. A total of 24 companies representing nine different countries have come to the support of the Center so far this year. We are again pleased to note three new additions to RIC's family of benefactors. Contributions were received from the following (the number in parentheses indicates the number of years the company has supported RIC):

- Apache Chemical, Inc., U.S.A. (1)
- W. R. Grace and Co., U.S.A. (9)
- Hitachi Magnetics Corp., U.S.A. (3)
- Indian Rare Earths, Ltd., India (8)
- Inland Motor Division, Kollmorgen Corp., U.S.A. (1)
- Kolon Trading Co., Inc., U.S.A. (4)
- Mischmetal & Flints, Private, Ltd., India (1)
- Mitsubishi Chemical Industries, Ltd., Japan (4)
- Rare Earth Products, Ltd., United Kingdom (5)
- Reactor Experiments, Inc., U.S.A. (7)
- Ronson Metals Corp., U.S.A. (9)
- Shin-Etsu Chemical Co., Ltd., Japan (7).

MEETING

An international conference on the Physics of the Metallic Rare-Earths and Actinides will be held at Saint Pierre de Chartreuse, near Grenoble, France, from August 30-September 2, 1978. A preliminary list of topics includes: intermediate valence, magnetism, phase transitions, electronic structure, amorphous materials and liquids. Each subject will have presentations by guest speakers. Particular aspects will be developed in shorter talks or poster sessions. The total number of participants will be limited to about one hundred. The Conference is organized by B. Coqblin (Orsay), A. Fert (Orsay), Rémi Lemaire (Grenoble) and is sponsored by the French Physical Society. Further information can be obtained from:

Conference on the Physics of the Metallic Rare-Earth and Actinides, Laboratoire de Magnetisme du C.N.R.S., 166 X, 38042 Grenoble, France.

RE's in the News

Laser Host Developed

An Air Force project has produced forty rods of anisotropic yttrium aluminate doped with neodymium. This material could possibly replace YAG:Nd in laser systems because of smaller thermal losses and it does not need external equipment to polarize the laser emission.

Expands Magnet Production

Th. Goldschmidt AG has increased its capacity to produce rare earth-cobalt alloys in powder form for use in permanent magnets to 50 tons per year.

Superconductivity

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spin exchange interaction parameter and the temperature dependence of the exchange scattering of the conduction electrons by long-lived solute spins, 3) derive, in favorable cases, information pertaining to the energy level structure of rare earth ions in the crystalline electric field of their superconducting metallic host, and 4) observe magnetic-nonmagnetic transitions of an impurity induced by the application of an external pressure or variation of the composition of a binary alloy matrix." A strong point in favor of this technique is that T_c versus impurity concentration and specific heat jump versus T_c are relatively easy measurements to make and yet the detailed shapes of these curves are extremely sensitive to the magnetic state of the impurity.

RE Volumes

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bonding of 4f and 5f series organometallic compounds (Vol. 25). Cyclooctatetraene, cyclopentadiene, alkyl, aryl, allyl and arene complexes of the rare earths and actinides are discussed (157 ref.).

In "Structure and Bonding in Highly Coordinated Lanthanide Complexes" S. P. Sinha discusses the factors which influence the formation of rare earth complexes (Vol. 25). The structure and bonding of rare earth compounds with coordination numbers of 3, 4, 6, 7, 8, 9, 10, and 12 are reviewed. Complexes with mixed coordination are also discussed (231 ref.).

G. Blasse has reviewed the influence of charge-transfer and rydberg states on the luminescence properties of lanthanides and actinides (Vol. 26). The effects of charge transfer and 4f-5d states on the

Critical Thermodynamic Reviews

J. G. Travers, I. Dellien and L. G. Hepler have gathered, critically evaluated, calculated and tabulated thermodynamic properties, related equilibrium constants and standard potentials for compounds and aqueous species of scandium [*Thermochim. Acta* 15, 89-104 (1976)] and L. G. Hepler and P. P. Singh have done the same for lanthanum [*Thermochim. Acta* 16, 95-114 (1976)]. Both papers limit their scope to the inorganic compounds and complexes of the elements. References are cited and methods of calculations are described so that interested readers can check calculations and come to their own conclusions.

Dynamite Application

A feasibility study of a process to treat flue gas from red water incineration has been completed by J. Happel and M. A. Hnatow [AD/A 022,037 (February 1976)]. Red water is a waste product from the production of TNT and a suitable means of disposal was sought to prevent air pollution. In the scheme devised rare earth-based catalysts are used to convert nitrogen and sulfur compounds which result from red water incineration to oxides of the form NO_x and SO_x . These oxides are then reduced by carbon monoxide to N_2 and S_2 . The rare earth catalysts are particularly suited to this application because of their resistance to water vapor and oxygen poisoning and the fact that there are no side reactions to form COS or H_2S .

emission spectra of the lanthanides, the temperature quenching of lanthanide luminescence, and on energy transfer probabilities are discussed (112 ref.).

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