MLM--3663(OP)

DE91 002703

CHAPTER 7

SOLID STATE RADIOLUMINESCENT SOURCES USING ZEOLITES

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DISCLAIMER

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ABSTRACT

Inorganic zeolites show promise as an alternative to traditional tritium gas tube light sources. Greater proximity of tritium atoms and luminescing centers, as well as greater tritium loading density, have been obtained within the zeolite aluminosilicate matrix. Zeolites are in addition optically clear and radiation stable. The zeolite radioluminescence program is described. Procedures for obtaining light sources are presented and results are discussed.

INTRODUCTION

Traditional T_2 gas/phosphor/glass tube radioluminescent sources suffer from several factors which limit their typical output brightness to about 0.3 ft-Lambert (ca. 0.7 $\mu W/cm^2$) in the green. The self-absorption of beta-energy in T_2 is believed to limit the beta-power which strikes the phosphor [1]. The comparitively low achievable density of T_2 gas and the optical opacity of the commonly used phosphors are also considerable drawbacks. As an improvement upon the traditional design, therefore, an increased micro-proximity of T atoms and luminescing centers was desired. In addition, high tritium loading density (in a condensed phase) within an optically clear matrix was considered advantageous. As one approach to such improved RL sources, a number of new solid state zeolite matrices have been prepared, several of which have been loaded with tritium [2].

DESIGN

The zeolites used here are optically-clear micro-crystalline materials, with an extended negatively-charged aluminosilicate structure. Located within this structure are interconnected pores of molecular size dimensions. The pores of zeolites retain mobile positive ions (most commonly sodium) for charge balance. Linde types 4A and 13X were employed here, with general formulas $Na_2O:Al_2O_3:2SiO_2$ and $Na_2O:Al_2O_3:2.5SiO_2$, respectively [3]. Figure 1 shows a representation of the structures of both zeolites [4].

Zeolites have historically been used as drying agents. The pores of the structure have a strong affinity for small molecules such as water. When saturated with water the formulas for types 4A and 13X become $Na_2O:Al_2O_3:2SiO_2:4.5H_2O$ and $Na_2O:Al_2O_3:2.5SiO_2:6H_2O$, respectively [3]. In practice, dried zeolites absorb about 22% (4A) and 26% (13X) water by weight when exposed to water vapor at 100% R.H. and 300K [5].

Zeolites have also historically been used as ion-exchange media [6]. The sodium ions of the zeolite, because they are mobile, may be exchanged for other positively charged ions by immersion of the zeolite in an aqueous solution of the other ion [7]. Exchange is generally a facile process, where equilibrium partitioning of the available ions between lattice and solution is often attained in several hours in warm water.

Zeolites are considered to be sufficiently radiation-stable that they have commonly been used to remove radioactive ions from nuclear power plant waste water. More impressively, they have been employed in producing specific isotopes of value by neutron irradiation of zeolites loaded with lower isotopes. The activated isotope has then been eluted from the matrix by ion exchange even after a dose of 5×10^{23} thermal neutrons/cm^2 [8]. Zeolites have also commonly been employed in the capture of tritiated water HTO from the exhaust of tritium handling facilities and in the drying of streams of T_2 gas [9].

Given the properties above, zeolites appeared to hold much promise as radioluminescent sources based on tritium. Luminescent rare earth or transition metal ions were expected to exchange for the sodium ions present in the as-received material. Tritiated water would be strongly sorbed by the dried zeolite, providing a condensed phase of tritium beta-source within the matrix. The tritium and the luminescing ions would be within molecular dimensions of one another, thereby enabling an efficient use of beta-energy if the zeolite lattice were to propagate energy to fluorescing centers. Since the zeolite is an optically clear material, light created within the crystallite would escape. Finally, since the zeolite is considered radiation stable, a radioluminescent product would have significant longevity.

EXPERIMENTS AND RESULTS

Linde types 4A and 13X zeolites were purchased from Alfa Products (Morton Thiokol, Inc.) as -600 mesh crystalline powder. The sodium ion (Na^+) present in the material was exchanged with various rare earth ions. A typical procedure entailed slurrying 1 gram samples of zeolite in 20 ml of water for 20 hr at 60°C with approximately 1.5 gram of dissolved rare earth nitrate salt. In this way the following exchanged zeolites were prepared: Ce:X, Pr:X, Nd:X, Sm:X, Eu:A, Eu:X, Gd:X, Tb:A, Tb:X, Dy:X, Ho:X, Er:X, Tm:X, Yb:X, and Lu:X, where all rare earths were in their trivalent states. Analyses of Eu:X, Tb:X, and Tb:A showed rare earth incorporation to be 76%, 63%, and 55%, respectively, on an equivalent ionic charge basis, the remainder being Na^+. These analyses were performed by dissolution of the samples in HF, followed by metals determination by inductively coupled plasma-driven atomic emission spectroscopy.

Preliminary evaluation of the above materials for fluorescence was performed with a UV lamp emitting at 365nm. The Eu- and Tb-loaded materials fluoresced most strongly in the visible, the former red and the latter yellow-green. The Nd-exchanged material should fluoresce at around 1060nm in the near-IR. The Eu:X and Tb:X samples were chosen for further investigation with tritium.

Red Light

Eu:X, 52 mg, was placed in a glass ampoule and dried by evacuation to <50 millitorr at 400°C for 1 hour. The vapors above degassed liquid tritiated water (99% pure T_2O) were then allowed to expand into the ampoule and sorb onto the zeolite (which acts as a "pump" for water vapor). The zeolite was cooled for 2 minutes to 77K to enhance the pumping speed. Active cooling was removed and the collected T_2O ice allowed to melt; water was noted to "supersaturate" the zeolite, that is, zeolite crystallites were surrounded by liquid T_2O water. In this state, the matrix emitted 0.9-1.0 ft-Lambert of red light as measured by a Minolta model LS-110 photometer, an instrument corrected for the human photopic response curve. The "supersaturated" zeolite was then warmed to 40°C while the T_2O source was frozen at 77K. After 5 minutes, both active heating and cooling were removed and the materials allowed to equilibrate overnight. The zeolite powder, now loosely flowing but "saturated" with about 36 Ci of tritium as T_2O vapors, emitted 0.50 ft-Lambert red light.

Although the emission spectrum was not measured, it is presumed that the product Eu:X:T_2O emits in narrow atomic lines around 620nm, as has been shown previously for UV excitation of Eu:X [10]. Efficiency of the response of the photopically-filtered light meter at 620 nm is ca. 30% of that at the maximum around 550 nm. The energy emitted as visible light from the red source is thus approximately equivalent to that of a 1.5 to 3.0 ft-Lambert lamp emitting in the green.

Yellow-Green Light

53 mg of the Tb:X material was taken into a freshly prepared and cleaned ampoule. This material was dried in a vacuum of <50 millitorr for 3 hours to 335°C and then brought into contact with the vapors of freshly-degassed pure T_2O. Within a day, luminance of the sample reached 0.65 ft-L. Over the next two weeks, as the sample became saturated with T_2O, output grew to 0.77 ft-Lambert. This light output was also measured via a Minolta model LS-110 instrument. Total tritium content at saturation was estimated to be 36 Ci. It is presumed that the Tb:X:T_2O material emits at around 550nm, as shown for UV excitation of Tb:X [10].

An alternate method for the preparation of Tb:X:T_2O entailed heating Tb:X:H_2O in the presence of T_2 gas. A temperature of 250-400°C was required to drive the exchange of hydrogen isotopes between sorbed water and the diatomic T_2 gas. 50mg of Tb:X:H_2O was immersed in 1 atm of T_2 gas within a 3 ml tubular volume. An additional 17 ml tubular volume (ca. 3 mm interior diameter) of T_2 was separated from the sample volume by a 10 micron filtration element and a valve. Three exchange heatings were performed with valve open for 1 hour at 400°C, for 16 hours at 240°C, and for 87 hours at 380°C, each time with fresh T_2 gas in the volumes. The output brightness from the sample grew progressively upon each exchange run, attaining 0.2 ft-Lambert after the third run. As this was

substantially lower than that predicted (0.5 ft-Lambert) for equilibrium exchange with all the T_2 available in the three runs, it was concluded that the exchange process was made inefficient by limited diffusion of gas between the small and large volumes across the filter.

No diminution of the light outputs for either the Eu- or the Tb-based lamps was observed over at least several weeks. This is consistent with the radiation-hardness of zeolite.

DISCUSSION

Brightness levels from the solid state zeolite powders surpassed those of commercially available tritium lamps, and approached the 1 ft-Lambert level. [This brightness compares to ca. 10 ft-Lamberts from the white paper on which you read this report under typical room light or which appears on an average computer terminal.] The fact that the brightness gains in the zeolite design are modest, given the sizable amount of tritium sorbed onto the samples, suggests that the energy from the beta emission of tritium is not being effectively coupled to the luminescing rare earth center. This may not be too surprising in retrospect, given the fact that the bulk of the beta energy will be dissipated in the zeolite lattice (range of the beta being ca. 0.5 μm in the lattice [11]) and given the electrically insulating nature of the lattice. Presumably there are few excited electronic energy levels in the lattice close to those 5D levels of the rare earths which emit the visible radiation of interest, or those levels are not commonly populated during energy loss mechanisms from the beta particle, or there is poor resonance between the excited zeolite states and the rare earth 5D levels [12]. Combinations of other zeolite lattice types (of which there are dozens) with other rare earths, possibly with the inclusion of small organo-ligands within the lattice to increase overlap, could provide a much brighter radioluminescence.

Brightness from the zeolite powders also appeared limited because of internal reflectance losses within the powder column. Whenever a gap was created within the column, a substantially increased brightness was apparent from that gap: internal emissions were collected there and reflected out of the column. For this reason, dispersion of the powder in polymers or clear matrix of similar refractive index was considered desirable. Optically clarified dispersions were obtained with non-tritiated zeolite samples in methylmethacrylate (MM) and styrene-butadiene (SB) copolymer (from methylene chloride solvent). When these polymers were cast around Tb:X:T_2O samples, luminance from the dried films was small, quickly decreased over several days, and the polymers were visibly darkened by the radiation field within 2 (MM) to 7 (SB) days. It is felt that most of the T_2O escaped from the samples into the dry argon atmosphere of the glove box used for the preparations. Incorporation of a solidified beta source, such as tritiated methane or acetylene polymerized internally within the zeolite structure, could enable a stable dispersion. Zeolites which bind water more strongly than those employed here would also enable such a dispersion and thus additional brightness.

ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy under Contract No. DE-AC04-88-DP43495. The authors specifically wish to thank L. E. Leonard of the U.S. Department of Energy for encouragement, enthusiasm, and support.

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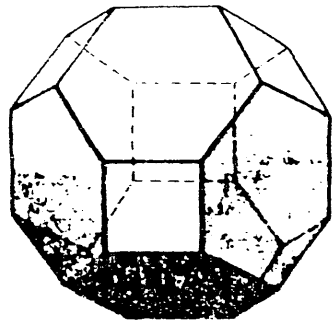
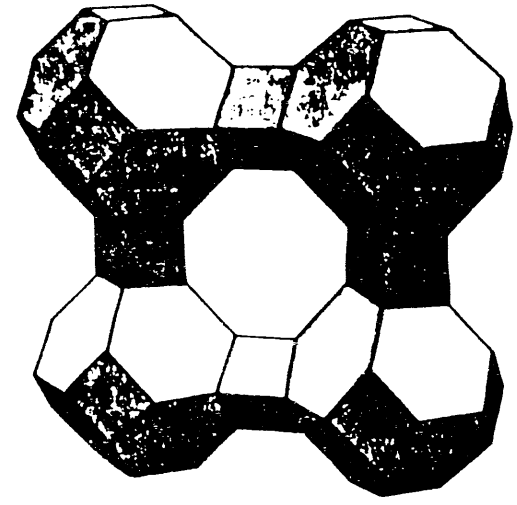
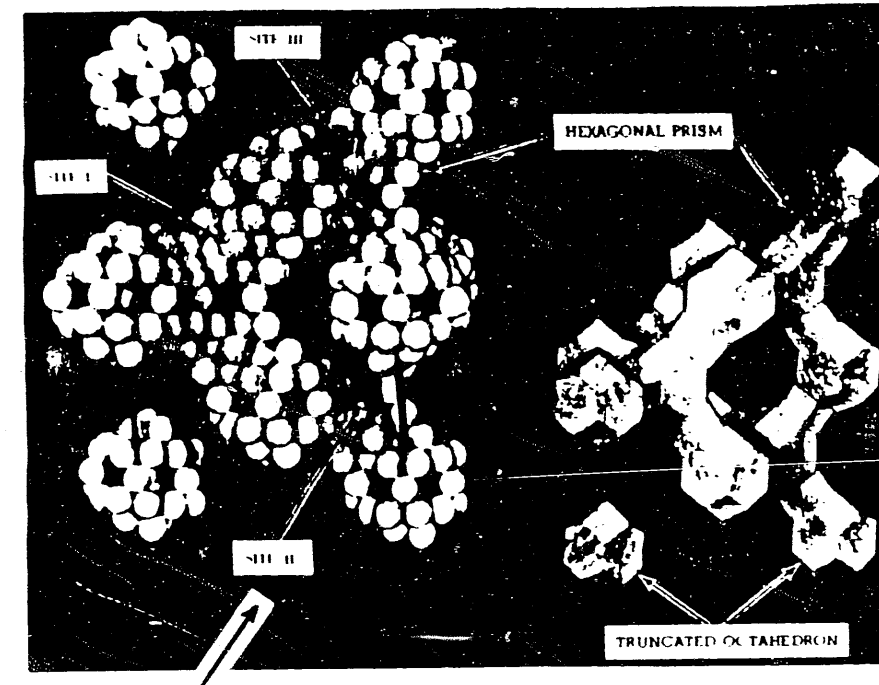
FIGURE 1. REPRESENTATIONS OF THE LATTICES OF ZEOLITES TYPE A & TYPE X



BASIC BUILDING BLOCK (TRUNCATED OCTAHEDRON)



TYPE A LATTICE



Cation Sites

TYPE X LATTICE

[Each vertex represents a Si or Al atom surrounded by 4 O atoms]

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