RARE-EARTH INFORMATION CENTER INSIGHT

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Heavy Metal Fluoride Glass Optical Fibers

Heavy metal fluoride (HMF) glasses have received a great deal of attention, since the early 1980's, as the new generation optical fibers. There is better than an even chance that these materials will have an enormous impact on the rare earth industry in the mid-1990 to the end of this century.

The HMF glasses were discovered by accident by M. Poulain, J. Lucas and co-workers at the University of Rennes in early 1974, when they tried to prepare a compound containing ZrF_4, BaF_2, NaF and NdF_3 with the $SmZrF_7$ type crystal structure. Later they noted that the transparency of these HMF glasses extended into the infrared region. It was realized that these glasses might make excellent ultralow-loss fiber optical materials.

Subsequent research showed that one of the better compositions is ZBLAN: $53ZrF_4$-$20BaF_2$-$4LaF_3$-$3AlF_3$-20NaF (in mol%). This material has a predicted attenuation coefficient (also called the optical loss) of $\sim10^{-2}$ dB/km at 2.55 µm, which is about an order of magnitude lower than silica glasses. An optical loss of 1 dB/km means that 1% of the incident light is transmitted through a 20 km length (the other 99% is lost), a 0.1 dB/km value corresponds to a 1% transmission through 200 km. Furthermore, since the HMF glasses have a lower refractive index the dispersion is lower. Research is concentrating on getting ZBLAN materials purer in order to attain the theoretical attenuation value. The best values reported for the optical loss are 0.9 dB/km at the Naval Research Laboratory (Washington, DC) and 0.7 dB/km at NTT Laboratories (Japan). Values of ~4 dB/km are routinely achieved. The theoretical limit is 0.035 dB/km, assuming the transition metal ions (Fe^{2+}, Co^{2+} etc.) the lanthanide ions with unpaired 4f electrons, and the hydroxyl ion (OH^-) were present in concentrations of 0.1 to 5 ppb (part per billion). The worst ions (listed in order of decreasing attenuation coefficient) at 2.55 µm are: OH^-, Cu^{2+}, Nd^{3+}, Sm^{3+} and Fe^{2+}.

If this theoretical value were achieved, ZBLAN could be used to transmit information over a distance of 1,500 km without a repeater, an improvement of a factor of ~6 over the best silica glass optical fibers. Other potential uses, which are more likely to be commercially realized before the 1,500 km optical fiber cable, are listed below and exploit ZBLAN's transparency in the IR region: 1) prisms and lenses for use out to 6 - 10 µm; 2) fiber optic waveguides for remote sensing and imaging out to 5 µm; 3) optical fibers for power delivery in the mid-IR range, e.g. HF laser at 2.5 µm

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or Er^{3+} laser at 2.9 μm; and 4) window materials for high energy lasers, e.g. HF laser. Item 3 is of special interest in surgical applications since water in tissues absorb strongly at 2.5 and 2.9 μm. For these four applications the 4 dB/km ZBLAN glass presently available is probably adequate.

What does this portent for the rare earth industry? A new market which will complement the neodymium permanent magnet market, which is expected to yield excess quantities of the other light lanthanide materials in the 1990's as this market grows. The lanthanum volume in this HMF glass market is not expected to be large enough to absorb all of the excess lanthanum, but it will help to reduce the surplus. The dollar value of the lanthanum oxide produced for this application will be extremely high because of high purity requirements, i.e. neodymium and samarium concentrations at 1 ppb or less and praseodymium and cerium concentration limits somewhat higher. This means the rare earth producers involved with today's "pure" La_2O_3 will need to improve their current processing techniques by a factor of 100 to 10,000. It is unlikely that solvent extraction alone will yield La_2O_3 of the required purity, and more than likely ion exchange capabilities will also be needed. Special clean rooms will be needed to prevent external contamination during the final processing stages. Furthermore, high purity conversion processes for making the LaF_3 will be required. Current techniques used by industry will not work. The best method in use today is the direct hydrofluorination method of reacting anhydrous HF gas with La_2O_3 at low temperature, followed by melting in a platinum crucible under an Ar-HF gas atmosphere. (LaF_3 melts at ~1500°C).

ZBLAN is not a shoo-in. Other problems in addition to the purity requirements need to be addressed. Although ZBLAN can easily be prepared, the temperature range for drawing the glass fibers in the viscous range is narrow, but good quality control in the processing should take care of this short coming. The other major concern is the poor chemical durability. HMF glasses are attacked by water which can produce surface flaws and accelerate their growth during stress. But progress is being made in producing flaw-free surfaces and surface coatings impervious to water.

The future looks good for the rare earths, especially lanthanum, in the optical fiber market of the 1990's, which is estimated to be in excess of a billion dollars. The rare earth portion has a potential of being one of the better rare earth markets, dollar-wise, going into the 21st Century.

Chinese Become Largest RE Producer!

According to China Rare Earth Information (February 1988) the People's Republic of China became the world's largest producer of mined rare earths in 1987, producing 15,100 mt. Since this exceeded the U.S.A.'s 1986 production of 14,500 mt, they claimed first place. This claim may or may not be valid, since we do not have the final figures for the 1987 U.S.A. production. Irregardless, the Chinese are either in first place or are an extremely close second. If they are not first in 1987, more than likely they will be in 1988. Approximately 45% of this 15,100 mt was exported.

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