Reduction of Impurities in Fluoride Glass Optical Fiber

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Reduction of Impurities in Fluoride Glass Optical Fiber

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A sublimation purification technique was developed for fluoride fiber materials, ZrF_4, BaF_2, GdF_3, and AlF_3. Using these purified materials and a "build-in casting" method, the low-transmission-loss of 8.5 dB/km at 2.12 μm was obtained, which is the lowest loss in an infrared ray transmitting fluoride glass fiber. The impurity level of the fiber was estimated as below 0.5 ppm by loss-factor analysis.

Fluoride glass can be considered as a promising candidate for an extremely low transmission loss media in the wavelength region longer than 2 μm.[1–3] There have been several reports on the characteristics of fluoride glass fibers.[4–6] Tran and his co-workers reported on BaF_2–LaF_3–ZrF_4–PbF_2–AlF_3–LiF glass fibers,[4] Ohsawa and his colleagues on BaF_2–LaF_3–ZrF_4–NaF–AlF_3 fibers.[5] The authors have reported on BaF_2–GdF_3–ZrF_4–AlF_3 fibers with transmission loss of 21 dB/km achieved by developing a "build-in casting" method.[6] There are still problems to be solved associated with the development of low loss optical fiber, such as scattering loss caused by crystallization during the fiber drawing process, absorption loss by OH ions and transition metal impurities in the glass. Among these, metal impurity contamination is one of the most serious because transition metal ions have huge absorption bands in the wavelength range of interest. It was determined that Fe^{2+}, Cu^{2+}, and OH^- are the most troublesome impurities in the 2.5 μm band. Therefore, material purification is indispensable for producing low loss fiber.

This letter presents a reduction of impurities in starting fluoride materials and fabrication of low loss fiber with 8.5 dB/km using these materials. A loss factor analysis is also described to obtain an indication of further reduction in transmission loss.

Starting materials, ZrF_4, BaF_2, GdF_3, and AlF_3 were purified by sublimation under low pressure at high temperature. Figure 1 shows a diagram of the sublimation system. Raw materials, ZrF_4 and AlF_3, were sublimated respectively at 900°C and at 1000°C in a dry Ar atmosphere at 1–3 mmHg, while BaF_2 and GdF_3 were purified by sublimating out transition metal impurities. The residuals were provided for fiber fabrication.

A mixture of 31.7 mol% BaF_2–3.8 GdF_3–60.5 ZrF_4–4AlF_3 for core glass and of 30.7 mol%BaF_2–3.7 GdF_3–58.6 ZrF_4–7.0 AlF_3 for cladding glass were each melted at 900°C for 2 hours in a gold crucible. The preforms with core-cladding structure were prepared by a specially developed "build-in casting" method:[6] the cladding glass melt was cast into a cylindrical brass mold which had been preheated at about glass transition temperature, and was then upturned. The melt in the central part of the mold was poured out, and the core

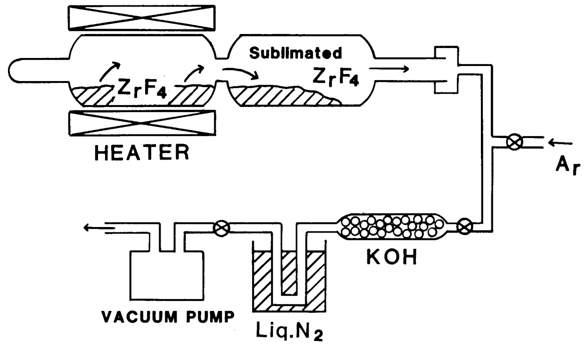

Fig. 1. Diagram of sublimation system.

glass melt was instantly cast into the cylindrical central hollow part and then annealed. Thus, the preform was obtained with a waveguide structure made of fluoride glass in both core and cladding parts. This preform, jacketed with a Teflon-FEP tube, was zonally heated by an electric furnace and drawn into a fiber. Core diameter was 35 μm, cladding diameter was 145 μm, the relative refractive index difference was 0.25%, and fiber length was 150 meters.

Optical loss spectra for the fibers were measured in the 0.7–4 μm wavelength region using a tungsten-iodine lamp for 0.7–1.7 μm and a platinum lamp for 1.7–4 μm as light sources, a grating monochromator, and an InSb detector. Measurement was accomplished by a cut-back method under launching conditions of 0.05 N.A. and cladding mode stripping using α-Bromonaphthalene which has a higher refractive index than cladding glass.

The impurity ion concentration in a fiber could be estimated by the best match between the measured spectral loss and the synthesized impurity absorption loss based on the experimental absorption curve for the individual ion impurity in the BaF_2–GdF_3–ZrF_4–AlF_3 glass.[7] Scattering loss was estimated by extrapolating the scattering loss value measured at 0.633 μm for a fluoride glass rod in accordance with the reciprocal second power of wavelength (λ^{-2}).

Figure 2 shows a transmission loss spectrum for the fiber and the result of the loss-factor analysis. The absorption band at around 1 μm can be assigned mainly to Cu^{2+} absorption. The large absorption band at 3 μm is assigned to OH^- absorption and the two small peaks at 2.25 and 2.45 μm are assigned to combined tones between OH stretching vibration and glass matrix vibration of Zr–F and Ba–F, respectively.

The minimum loss of 8.5 dB/km appeared at 2.12 μm. Minimum loss for the fiber prepared using conventional raw materials had been located at 2.55 μm.[6] It can be noted that the minimum loss wavelength shifted to a slightly shorter wavelength range, since Fe^{2+} concentration was fairly reduced by the present sublimation purification. Table 1 shows the estimated impurity concentrations in the fibers prepared with the purified materials, compared with those prepared with the raw materials.[6] The content of Fe^{2+} is reduced to about 1/20 and Cu^{2+} to 1/3. It is noted that Fe^{2+} content is remarkably decreased by the sublimation technique. The total concentration of transition metal impurities was reduced from 1.88 ppm to 0.49 ppm for the present fiber. In order to reduce the impurities further, optimization of sublimation conditions, such as temperature and pressure, and decontamination during glass melting and casting processes should be attempted. This effort of removing the transition metal impurities together with lowering scattering loss and OH radicals, will accomplish even greater reduction of fiber transmission loss.

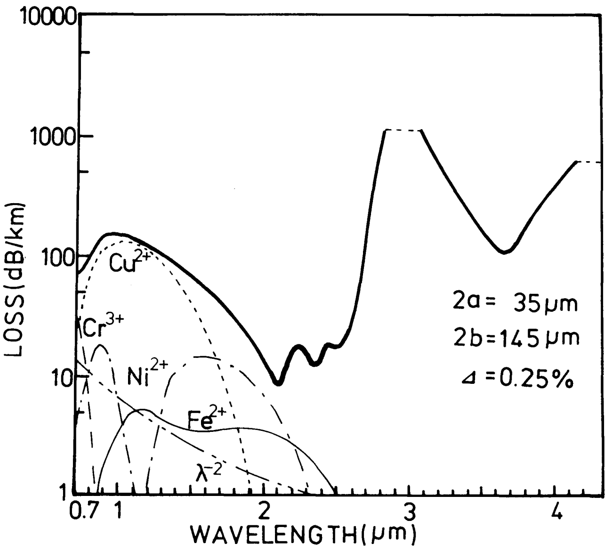

Fig. 2. Transmission loss spectrum for fluoride optical fiber and its loss-factor analysis.

Table I. Estimated impurity content (ppm)

	Fe^{2+}	Cu^{2+}	Ni^{2+}	Cr^{3+}
Fiber with raw material	0.79	0.81	0.10	0.18
Fiber with purified material	0.04	0.25	0.09	0.11

In summary, a sublimation purification technique was developed for fluoride fiber materials, ZrF_4, BaF_2, GdF_3, and AlF_3. Using these purified materials, the transition metal impurities were reduced below 0.5 ppm and a low loss fluoride fiber with 8.5 dB/km at 2.12 μm, which is the lowest loss in the infrared ray transmitting fluoride glass fibers, was prepared.

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