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Determination of Trace Iron in Raw Materials Used for Fluoride Glass Fibers by Neutron Activation Analysis

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Trace iron in seven kinds of raw materials used for fluoride glass fibers was determined by neutron activation analysis. Sub-stoichiometric neutron activation analysis of iron in $(NH_4)_2ZrF_6$, ZrF_4, and BaF_2 and instrumental neutron activation analysis of iron in YF_3, LaF_3, AlF_3, and NaF were carried out. Iron concentration in sublimated ZrF_4, BaF_2, YF_3, and LaF_3 was in the 11-76 ng g^{-1} range.

Transmission loss in fluoride glass fibers is greatly affected by trace amounts of 3d-transition metal impurities, especially by trace iron at the ng g^{-1} level.[1] Therefore, it is necessary to determine the level of trace iron in order to fabricate ultra-low loss fluoride glass fibers. The detection limit for iron as determined by spectral loss measurements of fluoride glass fibers is 100 ng g^{-1}.[2] Determination of trace iron in high-purity materials at a concentration of less than 100 ng g^{-1} by ordinary analytical methods is very difficult due to iron contamination from reagents and apparatus. Accurate analytical results for iron below the 100 ng g^{-1} level have not yet been reported. However, neutron activation analysis(NAA) is a highly sensitive and accurate technique for determining trace elements in high-purity materials. Trace amounts of copper and manganese in high-purity optical glass have also been determined by this method.[3] However, it has been reported that NAA is not suitable for determining levels of trace iron due to a paucity of the target nuclide ^{58}Fe(0.33%) and the fact that detection limit for iron is only 4-9 μg under a thermal neutron flux of 1.0×10^{13} n cm^{-2} s^{-1} after 1 h.[4] However, NAA can be used to determine trace elements using a thermal neutron flux of

3.0×10^{13} n cm^{-2} s^{-1} in a 265 h irradiation and a detection limit for iron of about 5-11 ng can be estimated under the above irradiation conditions. After irradiation for 265 h, the radioactivities of major and minor constituents are so large that chemical separation is frequently needed to determine trace iron. Substoichiometric neutron activation analysis(SNAA) is a useful NAA with a chemical separation method for determining trace elements.[5] When the half-life of a major radionuclide is shorter than that of $^{59}Fe(T_{\frac{1}{2}}=45.1$ d), which is the iron radionuclide used for the NAA of iron, instrumental neutron activation analysis(INAA) is available for determining trace iron.

In this paper, trace iron was determined by SNAA and INAA in seven kinds of raw materials used in the manufacture of fluoride glass fibers.

The raw materials were, $(NH_4)_2ZrF_6$, ZrF_4, BaF_2, YF_3, LaF_3, AlF_3, and NaF. Commercially available reagent grade $(NH_4)_2ZrF_6$ and high-purity NaF were used without further purification. High-purity commercially available ZrF_4, BaF_2, YF_3, LaF_3, and AlF_3 were used as well as sublimated samples of these materials. The sublimation was carried out in our laboratory.

A small piece of standard iron(4.0 mg) and raw materials(0.06-0.51 g) were packed in the same aluminum capsule and irradiated in a JRR-2 nuclear reactor at the Japan Atomic Energy Research Institute in a thermal neutron flux of 3.0×10^{13} n cm^{-2} s^{-1} for 265 h. After irradiation of YF_3, LaF_3, AlF_3, and NaF, short-lived radionuclides $^{90}Y(T_{\frac{1}{2}}=64$ h), $^{140}La(T_{\frac{1}{2}}=40.2$ h), $^{28}Al(T_{\frac{1}{2}}=2.2$ min), and ^{24}Na ($T_{\frac{1}{2}}=15$ h) were produced and the irradiated samples were cooled until matrix radioactivities had almost completely decayed. Gamma-ray spectra of the irradiated samples and the standard were measured using a coaxial Ge(Li) semiconductor detector with an effective volume of 30 cm^3 together with a 4096-channel pulse height analyser(4K-PHA) for 2×10^4 s - 3×10^5 s. Long-lived radionuclide ^{95}Zr ($T_{\frac{1}{2}}=65.5$ d)-$^{95}Nb(T_{\frac{1}{2}}=35.1$ d), $^{181}Hf(T_{\frac{1}{2}}=42.4$ d), and $^{131}Ba(T_{\frac{1}{2}}=11.7$ d) were produced by irradiation of $(NH_4)_2ZrF_6$, ZrF_4, and BaF_2 and trace iron in the samples could be determined only by chemical separation. SNAA of iron in $(NH_4)_2ZrF_6$, ZrF_4, and BaF_2 was carried out as follows: Two mg with iron carriers were added to the irradiated samples and dissolved in 46% hydrofluoric acid for ZrF_4 and 12 M-hydrochloric acid for $(NH_4)_2ZrF_6$ and BaF_2. Iron was extracted with methyl isobuthyl ketone(MIBK) in 7.5 M-hydrochloric acid and back-extracted with distilled water. The aqueous part was extracted with an excess amount of

cupferron into chloroform under 1 M-hydrochloric acid. The organic extract was washed with a mixture of 0.5 M-nitric and 0.5 M-hydrofluoric acids and back-extracted with 12 M-hydrochloric acid. The solution was evaporated and then wet-ashed with a mixture of nitric and sulfuric acids and hydrogen peroxide. The pH of the wet-ashed solution was adjusted to 5.0 with ammonium acetate and substoichiometric extraction was carried out with 2.7×10^{-2} M(1 M=1 mol dm^{-3}) cupferron into chloroform.[6] The irradiated iron standard solution containing two mg of iron carriers was in exactly the same way as was the substoichiometric extraction. Radioactivity of ^{59}Fe($E\gamma$=1099 keV) for the sample and standard was measured using the Ge(Li) semiconductor detector together with a 4K-PHA. The amount of iron in the samples was calculated by the comparison method of SNAA.[5]

The analytical results of iron in $(NH_4)_2ZrF_6$, ZrF_4, and BaF_2 by SNAA are shown in Table 1. Iron concentration of 76 ng g^{-1} in the sublimated ZrF_4 and 45 ng g^{-1} in the sublimated BaF_2 were determined by SNAA. The iron contents

Table 1. Analytical results of iron in raw materials used for fluoride glass fibers by substoichiometric neutron activation analysis

Sample	Grade	Sample weight/g	M_s b)/ng	a_s b)cpm	a_x b)cpm	M_x b)/ng	Iron concentration ng g^{-1}	
							Obtained	Mean value
$(NH_4)_2ZrF_6$								
1-1	Reagent	0.5106	18400	23.3	0.84	660	1290	1330 ± 57
1-2 a)	grade	0.5106	18400	18.5	0.70	700	1370	
ZrF_4								
1-1	High-	0.2183	13700	22.7	0.28	170	780	780
1-2 a)	purity	0.2183	13700	22.6	0.28	170	780	
2-1	Sublimated	0.1790	13700	22.7	0.020	12	67	76 ± 12
2-2 a)	sample	0.1790	13700	22.7	0.024	15	84	
BaF_2								
1-1	High-	0.0645	12900	12.4	0.027	28	430	440 ± 12
1-2 a)	purity	0.0645	12900	5.4	0.012	29	450	
1-3 a)		0.0645	12900	11.6	0.026	29	450	
2-1	Sublimated	0.3343	12900	12.4	0.013	14	42	45 ± 11
2-2 a)	sample	0.3343	12900	8.7	0.008	12	36	
2-3 a)		0.3343	12900	11.6	0.017	19	57	

a) Value of re-extraction in the same final aqueous solution.

b) Reference 5; $M_x = M_s \frac{a_x}{a_s}$, M_x: Iron content in sample, M_s: Amount of iron standard, a_x: Radioactivity of sample, a_s: Radioactivity of iron standard.

obtained with successive extractions from the same final aqueous solution were in good agreement and the substoichiometric extraction of iron with cupferron was found to be a highly reproducible analytical method. Iron concentrations in the sublimated ZrF_4 and BaF_2 samples were about 10^{-1} lower than those in the non-sublimated commercially available high-purity samples.

Table 2 shows the analytical results of iron in YF_3, LaF_3, AlF_3, and NaF by INAA. The results shown are the mean value for three replications. An iron concentration of 11 ng g^{-1} in LaF_3 was determined by INAA measurement for 3×10^5 s. The iron content in YF_3 and LaF_3 prepared by sublimation was lower than that in NaF. The iron concentration in the sublimated AlF_3 was about 10^{-1} lower than that in non-sublimated high-purity AlF_3. It was found that the sublimation technique is a useful method for removing trace iron from ZrF_4, BaF_2, and AlF_3. A detection limit for iron of 4 ng was calculated from the CURRIE equation.[7)]

Table 2. Analytical results of iron in raw materials used for fluoride glass fibers by INAA

Sample	Grade	Iron concentration
		ng g^{-1}
YF_3	Sublimated sample	40 ± 10
LaF_3	Sublimated sample	11 ± 4
AlF_3	High-purity	1180 ± 60
	Sublimated sample	190 ± 20
NaF	High-purity	440 ± 30

References

1) Y.Ohishi, S.Mitachi, S.Shibata, and T.Manabe, Jpn.J.Appl.Phys., 20, L787 (1981).
2) S.Mitachi, Y.Terunuma, Y.Ohishi, and S.Takahashi, J.Lightwave.Tech., LT-2, 587 (1984).
3) K.Kudo, K.Kobayashi, and T.Shigematsu, J.Radioanal.Chem., 27, 329 (1975).
4) P.V.Guinn, 7th Conf.Radioisotopes(Japan), 1966, 563.
5) K.Kudo and N.Suzuki, J.Radioanal.Chem., 59, 605 (1980).
6) J.Stary, J.Růžička, and M.Salamon, Talanta, 10, 375 (1963).
7) L.Currie, Anal.Chem., 40, 587 (1968).

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