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Preparation of Highly Pure Lithium and Sodium Fluorides Using Solvent Extraction

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Synopsis. LiF and NaF can be purified by solvent extraction. The impurity concentrations in the purified NaF are 2.5 $\mathrm{ng\,g^{-1}}$ for chromium, 60 $\mathrm{ng\,g^{-1}}$ for iron, 0.03 $\mathrm{ng\,g^{-1}}$ for cobalt, and 1.5 $\mathrm{ng\,g^{-1}}$ for copper. The concentrations in the purified LiF are 42 $\mathrm{ng\,g^{-1}}$ for nickel and 2.1 $\mathrm{ng\,g^{-1}}$ for copper.

For the fabrication of ultra-low-loss fluoride optical glass fibers (lower than 0.1 $\mathrm{dB\,km^{-1}}$), it is necessary to decrease the amounts of impurities to a level of 1 $\mathrm{ng\,g^{-1}}$. This is because the presence of more than 1 $\mathrm{ng\,g^{-1}}$ of a transition element in fluoride optical glass fibers causes transmission loss from the fibers.[1] LiF and NaF are used as raw materials in fiber production. Impurity concentrations of transition elements in LiF and NaF prepared by distillation and zone melting are at the 1 $\mathrm{\mu g\,g^{-1}}$ level.[2,3] Preparation of highly pure LiF and NaF in which transition elements are lower than 1 $\mathrm{\mu g\,g^{-1}}$ have not been reported yet.

In the determination of iron, copper, and nickel, chelate extractions of iron(III) with cupferron, copper(II) with dithizone, and nickel(II) with dimethylglyoxime have been used frequently.[4] The extraction technique can also be applied to the removal of iron(III), copper(II), and nickel(II) impurities from LiF and NaF, because lithium(I) and sodium(I) do not react with these reagents.

The determination of trace amounts of transition elements at 1 $\mathrm{ng\,g^{-1}}$ is difficult. Although ordinary analytical methods such as atomic absorption spectrometry and spark-source mass spectrometry, etc are sensitive to most elements, the application of these methods is limited when the concentrations of the transition elements are at a level of 1 $\mathrm{ng\,g^{-1}}$. Neutron Activation Analysis(NAA) is a highly sensitive method for determining transition elements and the determination of chromium, cobalt, and copper of an order of $\mathrm{ng\,g^{-1}}$ in silica glass by NAA has been reported.[5] This paper describes the preparation of highly pure LiF and NaF by solvent extraction, and the NAA of transition elements in the purified LiF and NaF.

Experimental

Reagents and Apparatus. Reagent grade of LiCl and $\mathrm{Na_2CO_3}$ were used as starting materials. Three chelate reagents (dithizone, cupferron, and dimethylglyoxime) were used without further purification. Highly pure 49% hydrofluoric, nitric, and hydrochloric acids, as well as ammonia, carbon tetrachloride, and chloroform were obtained commercially. Distilled water was produced by sub-boiling distillation. Radioactivity was measured by a Ge(Li) detector coupled with a 4096-channel pulse-height analyzer (4K-PHA), and a low-background gas-flow counter.

Tracer Experiment. $^{60}\mathrm{Co}(T_{1/2}=5.27\ \mathrm{y})$, $^{65}\mathrm{Ni}(T_{1/2}=2.52\ \mathrm{h})$, and $^{64}\mathrm{Cu}(T_{1/2}=12.7\ \mathrm{h})$ tracers were prepared by irradiation of small amounts of cobalt nitrate, highly pure nickel and copper metals in the JRR-2 nuclear reactor and the product was dissolved in 1 $\mathrm{mol\,dm^{-3}}$ nitric acid. $^{59}\mathrm{Fe}(T_{1/2}=44.6\ \mathrm{d})$ tracer($\mathrm{FeCl_3}$ in 0.5 $\mathrm{mol\,dm^{-3}}$ hydrochloric acid solution; radiochemical purity=99%) was imported from USA and was diluted before use. Ten μg of each tracer was added to the solution containing 10 g of LiCl or $\mathrm{Na_2CO_3}$. Then, ^{59}Fe(III), ^{60}Co(II) and ^{64}Cu(II), and ^{65}Ni(II) were extracted with cupferron into chloroform, dithizone into carbon tetrachloride, and dimethylglyoxime into chloroform, respectively. The radioactivity of the organic extract was measured and recovery for each element was calculated. Each recovery for extraction of iron(III) with cupferron at pH=0.4—6.1, cobalt(II) with dithizone at pH=4.0—6.5, nickel(II) with dimethylglyoxime at pH=9.0—10.0, and copper(II) with dithizone at pH=0.3—6.5 was more than 99%. Thus, iron(III), cobalt(II), and copper(II) can be extracted with the above chelate reagents at pH=4.0 and nickel(II) is extracted with dimethylglyoxime into chloroform at pH=9.0.

Preparation of LiF and NaF. LiCl (100 g) or $\mathrm{Na_2CO_3}$ (100 g) was dissolved in 100 ml of distilled water. The LiCl solution was adjusted to pH=4.0, and extractions were carried out with cupferron into chloroform and dithizone into carbon tetrachloride. The residual aqueous solution was adjusted to pH=9.0, and the nickel impurity was extracted with dimethylglyoxime into chloroform. The impurities in the $\mathrm{Na_2CO_3}$ solution were also extracted with the same reagents and at pH value as described above. A solution of 150 ml of 49% highly pure hydrofluoric acid was added to the residual aqueous solution and alkali metal fluoride was precipitated. The precipitate was aged for 1 d, washed with distilled water, dried in a vacuum oven at 100 °C for 2 d, and dehydrated at 400 °C for 5 h in argon atmosphere. The prepared LiF and NaF were identified by X-ray powder diffraction analysis.

Neutron Activation Analysis. LiF, LiCl, NaF, and $\mathrm{Na_2CO_3}$ samples (0.2—2.0 g) and chromiun, iron, cobalt, nickel, and copper standards (1.0 μg—4.0 mg) were irradiated in the JRR-2 or JRR-4 nuclear reactor at a thermal neutron flux of $3\text{—}8\times10^{13}\ \mathrm{n\,cm^{-2}\,s^{-1}}$. In order to determine nickel and copper, the irradiation was carried out for 5—20 min, while for chromium, iron, and cobalt the irradiation time was 265 h. After irradiation for 265 h, the irradiated NaF was cooled 30 d until undesired radioactivities of $^{24}\mathrm{Na}(T_{1/2}=15\ \mathrm{h})$ had almost decayed. The radioactivities of NaF and chromium, iron, and cobalt standards were measured by a Ge(Li) detector coupled with a 4K-PHA for $1\times10^4\text{—}3\times10^5$ s. The concentrations of chromium, iron, and cobalt were determined by the photopeaks from ^{51}Cr(320 keV), ^{59}Fe(1099 keV), and ^{60}Co(1332 keV). Trace amounts of nickel and copper were determined by the comparison method of substoichiometric radioactivation analysis. Carriers of nickel (0.5 mg) and copper (0.2 mg) were added to the irradiated samples, and the samples were dissolved in 0.1 $\mathrm{mol\,dm^{-3}}$ nitric acid. Substoichiometric extractions of copper with dithizone into carbon tetrachloride at pH 1.0 and nickel with sodium diethyldithiocarbamate into carbon tetrachloride at pH 9.0 were carried out.[6,7] The irradiated

Table 1. Impurity Concentrations in LiF, LiCl, NaF, and Na$_2$CO$_3$ by NAA

Element	Analytical result/ng g^{-1} a)						
	LiF-1	LiF-2-1	LiF-2-2	LiCl	NaF-1	NaF-2	Na$_2$CO$_3$
Cr	—	—	—	—	2.5±0.3	29±1.7	35±2.1
Fe	—	—	—	—	60±10	440±40	690±70
Co	—	—	—	—	0.03±0.01	9.6±1.0	0.31±0.03
Ni	42±4.5	190±9.5	570±29	150±7.5	<40	<40	<40
Cu	2.1±0.6	37±4.0	550±28	13±4.3	1.5±0.5	22±2.9	13±4.0

a) Mean value ± standard deviation for five determinations.

nickel and copper standards were treated with exactly the same substoichiometric extraction as was described for the sample. The radioactivities of the extracts for the samples and standards were measured by a low-background gas-flow counter for 20 min.

Results and Discussion

The analytical results for chromium, iron, cobalt, nickel, and copper in LiF, LiCl, NaF, and Na$_2$CO$_3$ are shown in Table 1.

Results for the elements are mean values for five determinations. LiF-1 and NaF-1 were prepared samples. LiF-2-1, LiF-2-2, and NaF-2 were analytical grade commercial samples. The impurity concentrations in LiF-1 and NaF-1 were lower than those in LiCl and Na$_2$CO$_3$, which were the starting materials for the preparation of LiF-1 and NaF-1, and purified LiF and NaF could be prepared by the solvent extraction method. The concentration in LiF-1 was 42 ng g^{-1} for nickel, and 2.1 ng g^{-1} for copper. These values were lower than those in LiF-2-1 and LiF-2-2 by a factor of 2.2×10^{-1} to 3.8×10^{-3}. The impurity concentrations in NaF-1 were 2.5 ng g^{-1} for chromium, 60 ng g^{-1} for iron, 0.03 ng g^{-1} for cobalt, and 1.5 ng g^{-1} for copper and these values were lower than those in NaF-2 by a factor of 3.0×10^{-3} to 8.6×10^{-1}. The 40 ng g^{-1} detection limit for nickel was due to the interference by the radioactivity of ^{24}Na.

It was found that solvent extraction is a useful method for the preparation of highly pure LiF and NaF.

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