Instrumental Achievements

Determination of Lithium and Niobium in Lithium Niobate by Inductively Coupled Plasma Atomic Emission Spectrometry after Fusion with Ammonium Hydrogensulfate

Tetsuya Ashino and Kunio Takada

Institute for Materials Research, Tohoku University, Aoba, Sendai 980, Japan

The photorefractive and piezoelectric properties of lithium niobate ($LiNbO_3$) crystals have been widely investigated. The Li/Nb ratios of crystals usually shifted from stoichiometry during the process of crystallization. It has therefore been necessary to develop a procedure for a high-precision determination of lithium and niobium in order to evaluate the constitution of $LiNbO_3$ crystals. Inductively coupled plasma atomic emission spectrometry (ICP-AES) is especially well suited for the determination of lithium and niobium, due to its high sensitivity and wide dynamic range. Ceramic samples were decomposed by acid under pressure using a PTFE pressure vessel[1,2], or fusion with alkali metal salts.[3,4] In order to develop a procedure for a simple, high-precision determination of lithium and niobium in $LiNbO_3$, a fusion method using ammonium hydrogensulfate (NH_4HSO_4)[5] was investigated and employed. Because this method is expected to yield a short sample-preparation, the effects of the flux were scarcely found based on the analytical values by ICP-AES.

Experimental

Apparatus

A Hitachi P-5200 dual monochromatic ICP emission analysis system together with a quartz concentric nebulizer was used. The operating conditions are listed in Table 1. The analytical lines used were selected based on various considerations. They showed the highest sensitivity and largest signal/background ratio in all of the spectral lines of lithium and niobium in the wavelength range from 175 to 900 nm; no interference lines were observed. Yttrium was used as an internal reference element.[6] For fusion of the samples, a fused quartz crucible with double caps (inner volume 20 ml, homemade)[7] was used. For acid decomposition under pressure, a PTFE pressure vessel with a stainless-steel jacket (inner volume 50 ml) was used.

Reagents

Lithium standard solution (0.100 mg/ml): lithium carbonate was dried for 3 h at 120°C and weighed

Table 1   Instrumental and operating conditions

HITACHI P-5200 dual monochromatic ICP emission analysis system		
Monochromator	1	2
Slit width (μm)	30	30
Slit height (mm)	10	10
Grating (grooves/mm)	3600	1200
Observation height (mm)	15	15
Rf power (kW)	1.0	
Argon gas flow rate		
Plasma gas (l/min)	12	
Nebulizer gas (l/min)	0.45	
(kPa)	160	
Auxiliary gas (l/min)	0.5	
Wavelength (nm)	Li I 670.784	
	Nb II 309.418	
	Y II 371.030	
	(as internal)	

(0.5323 g); it was then dissolved in 10 ml of 9 M H_2SO_4. After boiling until CO_2 was evaporated, the solution was diluted to 100 ml with water. A 10 ml aliquot of the solution was diluted to 100 ml with water for use. Niobium standard solution (1.00 mg/ml): 100 mg of metallic niobium was dissolved in 10 ml of 7 M HNO_3 and 5 ml of HF. Subsequently, 10 ml of H_2SO_4 was added, and the solution was heated to fumes of H_2SO_4. After cooling at room temperature, 1 g of tartaric acid and 1 ml of H_2O_2 were immediately added. The solution was diluted to 100 ml with water. Yttrium standard solution (4 mg/ml): 1.27 g of yttrium oxide was dissolved in 25 ml of 9 M H_2SO_4. The solution was diluted to 250 ml with water. NH_4HSO_4 was recrystallized from water, since black soot was found in it. Any impurity elements in NH_4HSO_4 before and after recrystallization were determined by ICP-AES; the results were given in Table 2. Both sodium hydrogensulfate $(NaHSO_4)$ and potassium hydrogensulfate $(KHSO_4)$ were also recrystallized. All of the reagents used were of analytical-reagent grade.

Samples

$LiNbO_3$: a High Purity Chemicals product (99% up), an Aldrich product (99.99%), and a sample prepared

Table 2   Impurities in ammonium hydrogensulfate before and after recrystallization

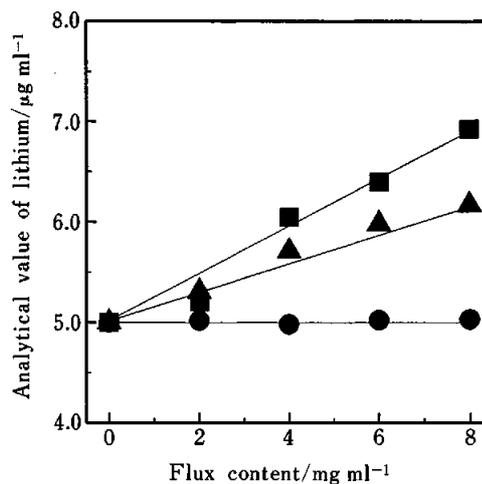| Element	Impulities found/μg g^{-1}	
	Before	After
Li	<0.05	<0.05
Nb	<0.01	<0.01
Al	0.4–0.6	0.09
Co	<0.05	<0.05
Cr	<0.05	<0.05
Cu	0.062	0.049
Fe	0.33–0.35	0.36–0.41
Mn	0.006	<0.005
Mo	<0.2	<0.2
Ni	<0.1	<0.1
Ti	3.8–3.9	1.4–1.5
V	<0.015	<0.015
Zn	0.31–0.43	0.15

Fig. 1   Effect of the flux content on the analytical value of lithium ●, ammonium hydrogensulfate; ▲, potassium hydrogensulfate; ■, sodium hydrogensulfate.

made in the Institute for Materials Research, Tohoku University, were analyzed.

Procedure

The fusion method: 100 mg of the sample was fused with 2 g of NH_4HSO_4 in a fused quartz crucible with double caps for 7 min.   After dissolving the fused salt with 20 ml of water, the solution was transferred into a volumetric flask.   Immediately, 10 ml of H_2SO_4, 1 g of tartaric acid and 1 ml of H_2O_2 were added, and the solution was diluted to 100 ml with water.   Next, 10 ml aliquot of the solution was transferred into another volumetric flask; subsequently, 4 ml of H_2SO_4 and 2.5 ml of yttrium standard solution were added.   Finally, the solution was diluted to 100 ml with water.   The sample solution was sprayed into ICP and the spectral intensities were measured.

Acid decomposition under pressure method: 100 mg of the sample was decomposed with 10 ml of HNO_3 and 5 ml of HF in a PTFE pressure vessel at 170°C for 15 h. The solution was transferred into a platinum dish; immediately, 10 ml of H_2SO_4 was added, and the solution was heated to fumes of H_2SO_4.   After cooling at room temperature, 1 g of tartaric acid and 1 ml of H_2O_2 were immediately added; the solution was then transferred into a 100 ml volumetric flask and was diluted to 100 ml with water.   The subsequent procedures were the same as in the fusion method.

Preparation of solutions for a calibration curve: from 0 to 8 ml of lithium and/or niobium standard solution were transferred into volumetric flasks; 5 ml of H_2SO_4 and 2.5 ml yttrium standard solution were then added to each solution.   Finally, the solutions were diluted to 100 ml with water.

Results and Discussion

Effect of flux

The effects of the flux content on the analytical value

by ICP-AES were examined.   The solution employed was prepared as follows: 5 ml of either a lithium or niobium standard solution was weighed into a volumetric flask; from 0 to 0.8 g of flux was then added stepwise. Subsequently, 5 ml of H_2SO_4 and 2.5 ml of yttrium standard solution were added.   Finally, the solutions were diluted to 100 ml with water.   The relations between the analytical value of lithium and flux content are shown in Fig. 1.   When $NaHSO_4$ or $KHSO_4$ was used as flux, the intensity of lithium was increased by a further addition of these sulfates.   However the intensity of yttrium was decreased.   For both $NaHSO_4$ and $KHSO_4$, lithium was not detected.   When NH_4HSO_4 was used, the intensities of both elements were independent of the quantity of the flux.   Therefore, for a determination of lithium by ICP-AES, NH_4HSO_4 is useful as a flux.   On the other hand, the analytical value of niobium was constant for all fluxes, since the behavior of the intensities of niobium and yttrium against the quantity of flux was similar.   Therefore, NH_4HSO_4 is suitable for a simultaneous determination of lithium and niobium by ICP-AES.

Mutual effects between lithium and niobium

The mutual effects between lithium and niobium on the analytical value by ICP-AES were examined.   The solutions were prepared as follows: 5 ml of either lithium or niobium standard solution was transferred into a volumetric flask; next, from 0.1 to 10-times the other elements was added stepwise as well as 0.4 g of NH_4HSO_4.   Then, 5 ml of H_2SO_4, and 2.5 ml of yttrium standard solution were added.   Finally, the solutions were diluted to 100 ml with water.   As a result, the intensity ratios of Li/Y and Nb/Y were similar. Therefore, no mutual effects between lithium and niobium on the analytical value by ICP-AES were found within this range.

Table 3   Analytical results of lithium niobate by acid decomposition under the pressure and fusion methods using ammonium hydrogensulfate

Method	Li, %	Nb, %	Atomic ratio (Nb/Li)
Fusion[a]	4.524	62.35	1.030
Acid	4.506	62.36	1.034
	4.516	62.28	1.030

Sample, High Purity Chemicals product (99% up).
a. $n=7$, Li: SD=0.00284, RSD=0.063%; Nb: SD=0.00303, RSD=0.049%.

Table 4   Analytical results

Sample	Li, %	Nb, %	Atomic ratio (Nb/Li)
A	4.475	63.45	1.059
	4.455	63.36	1.062
B	4.724	63.51	1.004
	4.726	63.64	1.006
C[a]	4.662	62.56	1.002
D[b]	4.613	62.65	1.015
E	4.719	63.24	1.001
	4.710	63.22	1.003

Sample A, Aldrich 99.99%. B, C, D, made in the Institute for Materials Research, Tohoku University. E, lithium oxide and niobium oxide 1:1 mixture, sintered.
a. $n=7$, Li: SD=0.00386, RSD=0.083%; Nb: SD=0.00339, RSD=0.054%.
b. $n=4$, Li: SD=0.00362, RSD=0.078%; Nb: SD=0.00184, RSD=0.029%.

Fusion method using ammonium hydrogensulfate and acid decomposition under the pressure method

After $LiNbO_3$ was decomposed by the fusion method using NH_4HSO_4 and the HNO_3 and HF mixture under pressure method, and the lithium and niobium concentrations were determined by ICP-AES. The obtained results are given in Table 3. The analytical values of lithium and niobium obtained by both methods were in good agreement. Both lithium and niobium could be determined to a precision of four significant figures based on the fusion method using NH_4HSO_4. Therefore, NH_4HSO_4 is a very useful flux, since a high-precision determination of lithium and niobium by ICP-AES is obtained.

Analysis of real samples

Real samples were prepared by the fusion method using NH_4HSO_4, and lithium, and the niobium concentrations were determined by ICP-AES. The results are given in Table 4.

In conclusion, the fusion method using NH_4HSO_4 is especially useful, since samples can be prepared in a short time, and no effects of flux content on analytical values by ICP-AES can be found. Further high-precision results are obtained.

References

1. H. Morikawa and T. Ishizuka, *Analyst* [London], **112**, 999 (1987).
2. T. Ishizuka, Y. Uwamino and A. Tsuge, *Bunseki Kagaku*, **34**, 487 (1985).
3. G. Müller-Vogt and W. Wendl, *Met. Res. Bull.*, **15**, 1461 (1980).
4. T. Ishizuka Y. Umemoto, A. Tsuge and T. Kamiyanagi, *Anal. Chim. Acta*, **161**, 285 (1984).
5. K. Matsumoto, Y. Misaki, K. Hayashi and K. Terada, *Fresenius' Z. Anal. Chem.*, **161**, 542 (1982).
6. JIS G 1258, "*Methods for Inductively Coupled Plasma Emission Spectrochemical Analysis of Steel*" Japanese Industrial Standard Committee, Tokyo, 1989.
7. K. Takada, H. Konno and T. Syoji, *Bunseki Kagaku*, **37**, T45 (1988).