derived by Sondheimer and later used by MAYER[6], where d = thickness of the film, ϱ = resistivity of the film, ϱ_∞ = resistivity of the bulk material having the same structure and approximately the same number of defects as the films, l_0 = mean free path of the charge carriers. The values of l_0 calculated by the two methods were found to agree satisfactorily.

Figs. 7 and 8 show the variation of the Hall mobility (μ_H) with film thickness and substrate temperature; the mobility being the product of Hall coefficient and conductivity: i. e. $\mu_H = R_H \sigma$.

Figs. 9 and 10 show the variation of the mean free path with film thickness and substrate temperature. The mean free path increases considerably with increasing film thickness and substrate temperature. Thus, as suggested before, the rise in conductivity was primarily due to a rise in the value of the mean free path.

The above studies clearly show that the substrate temperature at the time of deposition considerably modifies the film properties.

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[6] H. MAYER, Proc. of Int. Conf. "Structure and Properties of Thin Film", Bolton, Landing, New York, 225 (Sept. 1959).

Oxide and Hydroxide Activity Determination in Oxide Doped Lithium Fluoride

II. Total Oxygen Content Determination

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(Z. Naturforsch. 23 a, 351—354 [1968]; received 17 November 1967)

Results of independent measurements of thermodynamic activity (by a mass spectrometric method) and concentration (by neutron activation analysis) of lithium oxide in solid lithium fluoride are discussed. The analytical procedures involved as well as the potential uses of these experimental techniques for investigating fluoride-oxide systems are also described.

In a previous paper[1] dealing with the solubility of lithium hydroxide and lithium-oxide in solid lithium fluoride at temperatures ranging between about 600 °C and 760 °C, a method for determining the oxide and hydroxide activity (based on measurements of the partial pressures of water and hydrofluoric acid) was described. An indirect evaluation of the activity coefficient of lithium hydroxide was carried out, by utilizing the phase diagram of the system[2] LiOH – LiF, which indicates that its value is very near to one, in the range of the very diluted solid solutions we studied. Unfortunately, due to the lack of information on the solid state solubility of lithium oxide in lithium fluoride[3], activity coefficients of lithium oxide could not be calculated in the same manner, and the direct evaluation of the total oxygen content was necessary.

The present paper deals with the results of independent measurements of lithium oxide activity and concentration in lithium fluoride.

Experimental

1. Oxide and hydroxide activity determination

The oxide and hydroxide activity was determined according to the procedures outlined in a previous paper[1] by measuring the water and hydrofluoric acid partial pressures in equilibrium over a solid lithium fluoride sample. The sample (contained in a double walled silica cell) was doped with lithium oxide and hydroxide by keeping it for a period of about 40 hours at about 600 °C and $1 \cdot 10^{-6}$ Torr water partial pressure.

Immediately before quenching the sample was analyzed for oxide and hydroxide activities by measuring the water and hydrofluoric acid partial pressures.

The samples were quenched by streaming cold gas in the cell jacket. After quenching the cell was filled with inert gas at reduced pressure, sealed off, disconnected from the vacuum plant and transferred into a dry box filled with argon. There the cell was opened, the sintered sample milled and thereafter transferred into a small fused silica spheric capsule of 10 mm diameter at the end of a thin silica tube provided with a stopcock on the top.

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[1] G. TREVISAN and S. PIZZINI, Z. Naturforsch. 22 a, 651 [1967].

[2] G. SCARPA, Atti Accad. Naz. Lincei Rend. 24, II Sem. V Serie 476 [1915].

[3] Y. HAVEN, Rec. Trav. Chim. 69, 1505 [1950].

The sample was again heated at about 200 °C at $1 \cdot 10^{-4}$ Torr to remove the absorbed argon and finally the capsules were sealed off, disconnected from the tube and in-pile irradiated.

2. Preparation of standards for activation analysis

The lithium oxide — lithium fluoride samples used as reference mixtures for neutron activation analysis were prepared by heating at 600 °C under helium dried at the liquid nitrogen temperature after outgassing under high vacum at a temperature below 500 °C.

After milling, the samples were again heated at about 200 °C at $1 \cdot 10^{-4}$ Torr to remove the absorbed gas and finally the silica spheres were sealed off and disconnected from the tube.

The blanks of undoped lithium fluoride [4] were prepared in the same way.

3. Activation Analysis

The samples, sealed in silica vials as said before, were irradiated for two minutes in the PH 4 position of the Ispra I reactor. The unperturbated thermal neutron flux of the facility is $2 \cdot 10^{13}$ neutrons, cm^{-2} sec^{-1}. The epithermal component above the cadmium cut-off is only 1%.

The weight of both samples and standards varied between 51 and 138 mg. Two neutron flux monitors (thin aluminium wires with 210 μg of cobalt each) were placed around the capsule and the whole was wrapped in aluminium foil for better heat dissipation. No sign of melting was ever found.

After irradiation the capsules were opened and the LiF transferred to counting trays. The intensity of the 511 keV γ ray, formed by annihilation of the 649 keV positrons of F^{18} was measured by γ ray spectroscopy on a 3 × 3″ NaI(Tl) scintillation detector.

The output pulses were analysed on a 512 channels analyzer (model LABEN A 51). The radiochemical purity of the 511 keV γ rays was controlled by following its decay with time. The correct half-life of F^{18} (112 minutes) was always found.

The activity of the flux monitors was measured by γ ray spectroscopy of the 1332 keV γ ray of Co^{60}.

Quantitative measurements were done by the single comparator method [5]: eight standards with known oxygen content were prepared, irradiated separately together with neutron flux monitors, and finally counted. A counting rate of F^{18} per μg of oxygen under standard conditions of irradiation and counting was then calculated. The unknown samples were then irradiated together with flux monitors, counted in the same geometrical conditions and referred to the same irradiation conditions. Quantitative estimates were than done by comparison of the standardized counting rates.

Results and Discussion

The procedure reported utilizes a double nuclear reaction obtained during irradiation of LiF in a thermal neutron flux:

$$Li^{6}(n, \alpha)H^{3} \quad (1)$$

$$O^{16}(H^{3}, n)F^{18}. \quad (2)$$

The tritons produced by the first reaction have an energy of 2.74 MeV, which is sufficient for the activation of oxygen by the second reaction, which has an energetic threshold of only 0.3 MeV, and an activation cross section of about 600 millibarns for 2.7 MeV tritons. This method was first studied by Osmond and Smales [6]. Apparently it is ideally suited to the present problem for the following reasons:

a) its sensitivity is very high;
b) conditions of intimate mixing of lithium and oxygen (required by the short range of H^3 ions) are achieved, as a consequence of the type of the doping process, which leads to a solid solution;
c) no sample contamination due to atmospheric oxygen is possible before the in-pile irradiation, as the samples are sealed under vacuum and opened only after activation.

Possible sources of error and interferences in our application were considered.

Among the nuclear reactions leading to the formation of F^{18} only the reaction $F^{19}(n, 2n)F^{18}$ could have been a source of interference, due to the large mass of fluorine present. This interference was evaluated by irradiating a sample of NH_4F. The counting rate of F^{18} obtained corresponded to an apparent content of only 3.3 ppm of oxygen in LiF, and it was therefore neglected for this application, although it could easily be taken into account for analysis requiring a higher sensitivity.

As the neutron absorption of the matrix is rather high, different flux attenuations for different capsule dimensions could have been a source of error. In this work the capsule dimensions were not changed, but they were filled to a different extent. A previous work on the production of F^{18} in a nuclear reactor [7] suggests that the error due to different flux attenuations are in our conditions rather small and in fact

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[4] Lithium fluoride was delivered by Semielements Inc. Saxonbourg, Pa., U.S.A.

[5] F. Girardi, G. Guzzi, and J. Pauly, Anal. Chem. **37**, 1085 [1965].

[6] R. G. Osmond and A. A. Smales, Anal. Chim. Acta **10**, 117 [1954].

[7] M. Bresesti, A. M. del Turco, and A. Ostidich, Radiochim. Acta **2**, 49 [1963].

Standard	μg oxygen added	total sample weights (mg)	measured neutron flux	standard counting rate (SCR) *	SCR/μg oxygen (counts per minute)
1	0	51	$1.70 \cdot 10^{13}$	5000	—
2	288	115	2.08	44000	149
3	555	86.7	1.9	75000	135
4	870	128	2.0	131000	151
5	1540	120.8	1.7	235000	153
6	1780	136	2.0	226000	120 **
7	3620	120	1.7	495000	137
8	4320	118	2.0	601000	140

* Referred to a sample weight of 100 mg, a neutron flux of $2 \cdot 10^{13}$ neutrons cm^{-2} sec^{-1}, and at zero decay time.
** This value fell outside the standard deviation of the mean at 95% confidence level, and it was considered aberrant.

Table I.

Standard deviation of the means ±3.0 (2.1%)
SCR/μg oxygen mean 144.2
Standard error of a single measurement ±7.3 (5.1%)

eight standards with weights varying between 51 and 138 mg gave normalized counting rates which agreed within 5%.

The analysis were carried out by applying the single comparator method, already successfully used by one of the present authors [5].

In Table I the experimental results obtained in the irradiation of standards are reported. A standardized counting rate of 144.2 ± 3.0 cpm/μg oxygen was obtained from which an ultimate sensitivity of the order of 0.1 μg in our experimental conditions was estimated.

A standard error of ±5.1% was calculated for a single determination which was largely adequate to the precision requirements of the present work.

Fig. 1 shows the standardized counting rate (SCR) vs μg of oxygen added, showing points equally scattered on the calibration line, with no evidence of systematic trends. The same is true of plots of SCR vs. sample weights or neutron flux, which are not reported here.

A residual counting rate of 5.000 cpm was obtained without oxygen addition, from which an oxygen blank of 347 ppm was deduced.

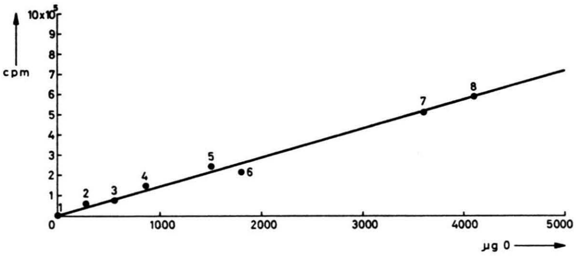

Fig. 1. Standardized counting rates (SCR) of standards vs. added weight of oxygen. Standard conditions are reported in the text. Numbers in the figure refer to number of the standard of Table I. (See Table I for experimental condition.)

Two samples were finally analyzed, which both showed an oxygen content of 820 ppm.

Table II reports the value of the molar fraction as measured by activation analysis and activity as measured from the partial pressure for a doped lithium fluoride sample and for a blank. The average activity coefficients for the lithium oxide-lithium fluoride solid solution results to be 0.8 at 605 °C, so that both oxide and hydroxide concentration could be deduced from equilibrium partial pressures measurements at least up to $X = 10^{-3}$ for both the oxide and hydroxide. It appears that the major con-

	Run	T (°C)	P_{HF} (torr) $\cdot 10^{-7}$	P_{H_2O} (torr) $\cdot 10^{-6}$	K_1 $\cdot 10^{-6}$	K_2 (atm)	a_{LiOH} $\cdot 10^{-6}$	a_{Li_2O} $\cdot 10^{-3}$	X_{LiOH} $\cdot 10^{-6}$	X_{Li_2O} $\cdot 10^{-3}$	γ_{Li_2O}	γ_{LiOH}	Total oxygen (ppm)
Sample	1	605±1	2.92	1.71	1.03	0.7176	6.0	1.16	6.0	1.33	0.87	1	820
	2	605	2.71	1.35			5.1	0.99	5.1		0.74	1	
	3	605	3.00	1.87			6.4	1.24	6.4		0.93	1	
	4	605	2.65	1.27			4.9	0.94	4.9	1.33	0.70	1	820
Blank		605±1								0.56			374

Table II.

K_1 = reaction constant for the reaction $LiF + H_2O \rightleftarrows LiOH + HF$.
K_2 = reaction constant for the reaction $2\,LiF + H_2O \rightleftarrows Li_2O + 2\,HF$.
X = molar fraction.
a = activity in activity units.

taminant of the solid (as could be however inferred from some extrapolations of the experimental data given for molten fluoride mixtures [8]) is the oxide.

Apparently its concentration is not so strongly dependent on the actual partial pressure of water as in the case of the lithium hydroxide, but depends on the initial carbonate content as well as on the rate of the pyrohydrolytic process.

These experimental results of course are not intended to represent a comprehensive treatment of the ternary system $Li_2O-LiOH-LiF$ (which has been treated throughout as two binary systems: $Li_2O-LiF/LiOH-LiF$), but a first look into the system as well as a new experimental approach for investigating systems of this kind in the range of the extremely high dilutions.

Moreover on the basis of the results obtained for the preparation of pure and doped lithium fluoride samples the requirements of a high temperature high vacuum process (for achieving halide samples with very low and known oxide contamination) can be quantitatively described.

It appears that the main parameters involved in determining the final oxide content are:

- the initial carbonate content (which fixes the lowest limit of contamination attainable);
- the partial pressure of water in the gas phase which in turn depends on the pumping speed of the vacuum system, as well as on the rate of production of water inside the system;
- the rates of the reactions:

$$2\,LiF + H_2O \rightleftarrows Li_2O + 2\,HF\,, \tag{3}$$

$$Li_2CO_3 \rightleftarrows CO_2 + Li_2O\,. \tag{4}$$

It follows that by knowing the performances of the vacuum plant and by monitoring the hydrofluoric acid and/or the carbon dioxide partial pressures, it is possible to evaluate the total oxide produced by means of the equations:

$$q_i = p_i\,S_i\,, \tag{5}$$

$$Q_i = \int_0^t q_i\,dt\,, \tag{6}$$

$$P_i = \int_0^t p_i\,dt\,, \tag{7}$$

$$Q_i = P_i\,S_i \tag{8}$$

where:

q_i = throughout [9] for the species in torr × 1 sec^{-1} i. e. in number of molecules pro second,

P_i = partial pressure of the i-th species in torr,

t = time of the experiment in seconds,

S_i = pumping speed for the species i calculated [9] in the same point where the pressure is measured (the pumping speed is considered constant over the whole range of p_i).

The integration of Eqs. (6) and (7) can be carried out graphically.

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[8] A. L. Mathews and C. F. Baes, ORNL-TM-1129 [1965].

[9] Handbook of Vacuum Physics, Edited by A. H. Beck, Pergamon Press, London.