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Crystal Characterization and Electrode Behaviour of Trifluorides of Lanthanum, Cerium and Praseodymium

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Doped and undoped crystals of the trifluorides of lanthanum, cerium and praseodymium were grown using the Bridgman method. Crystal qualities were assessed by neutron, gamma and X-ray diffraction methods. Numerous oriented crystal slices were used as membranes in fluoride sensitive electrodes. The experiments show that doping is necessary for the electrode function, whereas crystal quality and crystal orientation are of secondary importance.

Frant and Ross [1,2] were the first to apply lanthanum trifluoride as a membrane in a fluoride ion selective electrode. A large number of papers has been published on the subject of fluoride sensitive electrodes but information on possible correlations between crystallographic properties of the membrane and electrode behaviour appears to be lacking. The purpose of our investigation was to grow crystals of LaF_3, CeF_3 and PrF_3 with controlled amounts of impurities and to use crystals cut along defined crystallographic directions as membrane electrodes.

EXPERIMENTAL

Crystal growth. Commercial products of LaF_3, CeF_3 and PrF_3 of nominal 99.9 % purity contained small amounts of oxofluorides and oxides. They were purified by mixing the raw material with NH_4F and NH_4HF_4 and heating the mixtures up to 900 °C in a stream of purified argon. The following slow cooling was also carried out in an argon flow. The purified materials were used with and without dopants of divalent fluorides. The same technique was applied for the preparation of EuF_3 from Eu_2O_3. EuF_3 was subsequently reduced to EuF_2 using Si under similar conditions.[3] Crystals were grown from melts in glassy carbon crucibles which were lowered with speeds of about 1.8 mm/h using the Bridgman method and an A.D. Little MP crystal growth furnace. The crucibles were lowered into an afterheater to minimise temperature gradients and the final cooling was of ten hours duration. Helium of 0.3–0.4 MPa pressure was used as a protecting atmosphere.

X-Ray diffraction. Guinier photographs were taken of both of the raw material and of samples removed from selected parts of the single crystals. Line positions were measured using a high precision comparator and Si (a=5.43083 Å) as internal standard. CuKα_1 radiation (1.5405981 Å) was used. Further details in Ref. 4. Lattice constants were determined using the method of least squares.[4] Laue diagrams were used for orienting the crystals and slices of oriented crystals were cut using a diamond saw.

Neutron diffraction. Rocking curves were measured for a pure LaF_3 crystal with intervals of 2 mm along the cylindrical sample. The measurements showed that all the parts which

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yielded identical rocking curves appeared to be homogeneous with respect to optical properties. Hence, crystal slabs were selected for further examination using optical properties for preliminary screening.

Gamma diffraction. Rocking curves were measured using the 412 KeV Au-line and a diffractometer based on the principles described by Schneider.[5] The diffractometer is located at Risø.

Electrochemical methods. Nylon disks were attached to teflon tubes using standard O-ring technique. Oriented crystal slabs were polished using diamond paste down to 2μ grain size and glued to the nylon disks in such a way that the crystal completely covered a central hole of 1 mm diameter in the disk.

The crystal faces were covered with epoxy glue leaving only the interior and the exterior plane faces free to make contact with the aqueous solutions. The interior solution in the electrode was in all cases a mixture of 0.1 M KCl and 0.1 M NaF. The inner electrode was an Ag/AgCl electrode and the reference electrode was a Radiometer K 401 calomel electrode. A commercial Radiometer F 1052 F fluoride selective electrode was used for comparison. A Heterofrig ultrathermostat kept the electrochemical cells at 25 °C and a Radiometer PHM 84 potentiometer was used for measuring electrode potentials which were also recorded in time by a Toshin Electron X-t recorder. The potentials could be read to a nominal precision of 0.1 mV.

Solutions of molar concentrations in F^- of 10^{-1}, 10^{-2}, 10^{-3}, 10^{-4}, 10^{-5} and 10^{-6} were used for determining electrode response. The ionic strength was kept constant at 0.1 by addition of Cl^--ions. Also a 1 M NaF solution was used in this series of measurements. pH was approximately 7 in all the solutions.

RESULTS

The crystals prepared were cylindrically shaped, of diameter 1 cm and normally from 2 to 4 cm in length. In all cases, the *c*-axis was approximately perpendicular to the cylinder axis.

Table 1. Representative results from successful crystal growth experiments and results from lattice constant determination.

Material	Dopant	Conc. atomic %	a ($\sigma_a \times 10^4$) Å	c ($\sigma_c \times 10^4$) Å
LaF_3, JCPDP (32–483)			7.1871	7.3501
LaF_3, raw				
Pierce			7.1813(16)	7.3609(72)
Auer-Remy			7.1839(4)	7.3514(12)
LaF_3, purified			7.1821(7)	7.3511(21)
LaF_3	EuF_2	0.11	7.1840(6)	7.3534(16)
LaF_3	EuF_2	1.03	7.1849(4)	7.3541(12)
LaF_3	SrF_2	0.41	7.1838(5)	7.3538(16)
CeF_3, JCPDP (8–45)			7.112	7.279
CeF_3, raw				
Pierce			7.1161(32)	7.2955(18)
CeF_3, purified			7.1292(2)	7.2871(4)
CeF_3	SrF_2	9.10	7.1298(5)	7.3022(14)
PrF_3, JCPDP (6–325)			7.075	7.238
PrF_3, raw				
Auer-Remy			7.0774(2)	7.2396(9)
PrF_3	CaF_2	4.94	7.0629(2)	7.235(10)

Table 2. Results from measurements of rocking curves using γ-diffraction. Full width half maximum (FWHM) values are given. Another measure or perfection is the quantity $N(\max)/N(\text{total})$ where $N(\max)$ is the number of counts in the maximum and $N(\text{total})$ is the total number of counts in the peak, both values corrected for background. A low figure indicates the presence of more than one reflecting grain.

Crystal	Reflecting planes	FWHM (degree)	$N(\max)/N(\text{total}) \cdot 100$
Si	111		
LaF_3, pure	110	0.118	90
LaF_3, pure	002	0.045	56
LaF_3, 1 % EuF_2	110	0.085	49
LaF_3, 1 % EuF_2	002	0.065	40
CeF_3, 9.1 % SrF_2	110	0.039	98
CeF_3, 9.1 % SrF_2	002	0.068	67
PrF_3, 4.94 % CaF_2	110	0.115	98
PrF_3, 4.94 % CaF_2	002	0.055	74

Table 3. Electrode reponse of selected crystals. $e/mV = A + B \log[F^-]$. Regression lines calculated for $0 \leq -\log[F^-] \leq 5$. Speed of response is the time taken for establishment of a stable potential after changing $[F^-]$ by a factor of 10.

Electrode	Plane of contact	A	B	Coefficient of correlation	Speed of response
LaF_3, pure	(110)				
LaF_3, 1 % EuF_2	(110)	−11.83	58.20	0.99997	instantaneous
LaF_3, 1 % EuF_2	(001)	−9.69	56.56	0.99951	instantaneous
Radiometer		−55.73	57.01	0.99956	instantaneous
CeF_3, 9.1 %SrF_2	(110)	−10.66	56.85	0.99919	<2 min
CeF_3, 9.1 %SrF_2	(001)	−9.68	56.95	0.99931	<2 min
Radiometer		−57.67	58.06	0.99980	instantaneous
PrF_3, 4.9 % CaF_2	random	−8.37	55.98	0.99962	10 min
Radiometer		−54.79	55.99	0.99952	instantaneous
PrF_3, 1.5 % EuF_2	(110)	−9.42	57.75	0.99996	5 min
PrF_3, 1.5 % EuF_2	(001)	−10.88	58.18	0.99999	5 min
Radiometer		−57.43	57.32	0.99997	instantaneous

Some typical results of the crystal growth experiments are summarized in Table 1. This table shows that EuF_2 and SrF_2 tend to enlarge the unit cell dimensions of LaF_3 both in the *a*- and in the *c*-direction, whereas SrF_2 expands the CeF_3 lattice significantly only in the *c*-direction. The doping of PrF_3 with CaF_2 leads to a contraction of the *a*-axis whereas the *c*-axis is hardly changed.

Table 2 shows representative results derived from rocking curves obtained using 412 KeV γ-radiation. The instrumental resolution of the diffractometer was found to be 0.011°, as measured from the rocking curve of a silicon crystal. Thus, only fairly high degrees of mosaicity could be determined. The table shows that the mosaicities vary between 0.045° and 0.225° but no systematic trends are found.

Table 3 shows representative results from the measurements of the electrode behaviour of selected crystals. No electrode response was obtained from undoped crystals of LaF_3. Three orientations of crystals were tried: (001) and (110) and one undetermined plane

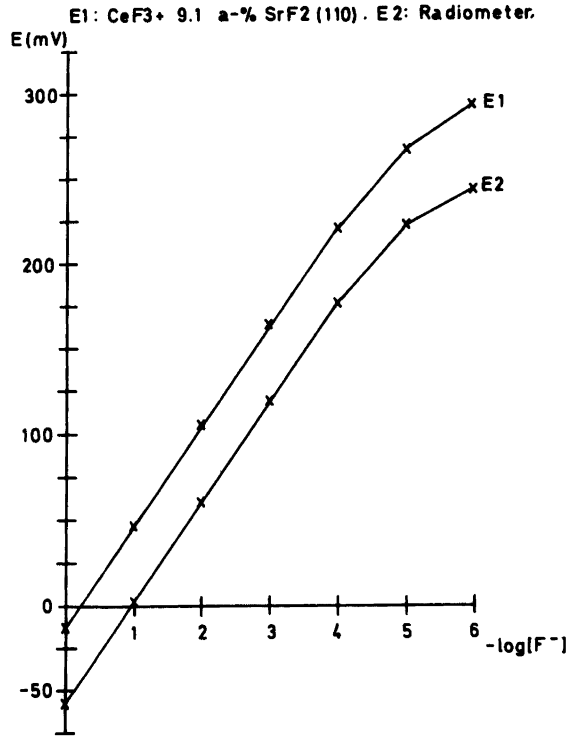

Fig. 1. Graph of E *vs.* -log[F^-] for the Radiometer electrode (LaF_3, EuF_2) and for one of our CeF_3, SrF_2 electrodes.

-log[F^-]	E1 (mV)	E2 (mV)
0.0	−14.3	−58.8
1.0	46.4	1.7
2.0	104.8	60.2
3.0	163.8	118.8
4.0	221.0	177.5
5.0	267.1	222.6
6.0	293.1	243.7

chosen at random were used as contact planes for the solutions. Apparently, the resistance over the membrane was too high to allow a consistent reading of the potentiometer.

In most cases, the crystals were cut parallel to the planes (110) and (001). Our results show that crystal orientation is of no importance for electrode response. Neither equilibrium nor kinetic properties were influences to any detectable amount by crystal orientation.

Using the assumption that activity coefficients, diffusion potentials etc. are constant for the test solutions the expected function of electrode potential with respect to fluoride ion concentration, [F^-], is as follows:

$$E=E_o-\frac{RT}{F}\ln[F^-] \text{ or}$$

$$E/\text{mV}=E'_o-59.16\log[F^-] \text{ or } E=A-B\log[F^-]$$

Table 3 shows that the electrode response is linear with respect to $\log[F^-]$ in the range $10^{-5} \leq [F^-] \leq 1$. The slope, B, is in all cases one to two mV less than the theoretical value: 59.16 mV. This behaviour is in accordance with observations of Durst[6] and with reported measurements of Durst and Taylor.[7] Calculation of slopes from data reported in the original Frant-Ross[2] patent give slopes of 55.6 mV (PrF_3) and 55.9 mV (CeF_3); values close to our results. Fig. 1 is a graph of E *vs.* $-\log[F^-]$ for the Radiometer electrode (LaF_3, EuF_2) and for one of our CeF_3, SrF_2 electrodes. The figure shows that the two electrodes differ very little in response.

The best electrodes were those made from EuF_2 doped LaF_3 and SrF_2 doped CeF_3. LaF_3 doped with 0.26 % SrF_2 reacted very slowly against changes in $[F^-]$ as did PrF_3 doped with CaF_2. The doping of PrF_3 with CaF_2 has to be fairly high in order to obtain any noticeable response, whereas doping with EuF_2 leads to much better electrodes although they are slower in establishing equilibrium than are the good LaF_3 and CeF_3 electrodes.

DISCUSSION

The crystals used in the commercial Radiometer electrodes are approximately 10 mm in diameter and 10 mm thick. Our membrane crystals are 1–3 mm thick and the interior solutions of the electrodes make contact to the crystal through a hole of diameter 1 mm. Size and thickness of the crystals seem to be of little or no importance for electrode function.

There has been some controversies over the structure of LaF_3 but two recent papers[8,9] seem to settle the problem in a definitive way. LaF_3 crystallizes in the Tysonite structure, space group $P\bar{3}c1$. Normally, however, the crystals are twinned around the c-axis so that the intensity distribution of X-ray and neutron reflections indicate hexagonal symmetry. Our crystals appear to be twinned too, but neither twinning nor orientation are of importance for electrode behaviour; only doping seems to matter.

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