ACTA CHEMICA SCANDINAVICA 19 (1965) 1376–1380

Phase Analysis Studies in the LiF-Nb_2O_5 System

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Two intermediate phases have been found to form in the system $LiF-Nb_2O_5$, in the temperature range 800–1200°C. The composition of one of them, $LiNb_6O_{15}F$, has been determined and its unit cell dimensions have been derived from single crystal data and the indexed Guinier powder pattern. For the second phase the composition is still somewhat uncertain and will here be given as $LiF \cdot 10\text{-}12\ Nb_2O_5$.

The thermal decomposition of $LiNb_6O_{15}F$ in argon was found to occur according to the following chemical formula:

$$3\ LiNb_6O_{15}F_{(s)} = NbOF_{3(g)} + 3\ LiNb_3O_{8(s)} + 4\ Nb_2O_{5(s)}$$

When the system $NaNbO_3-Nb_2O_5-H_2O$ was studied at high pressure and temperature a sodium niobium oxide hydroxide of the composition $NaNb_6O_{15}(OH)$ was observed as a very fibrous material.[1] In an attempt to synthesize the corresponding oxide fluoride, NaF and α-Nb_2O_5 were mixed in the mole ratio 1:3 and heated in a sealed platinum tube according to the technique developed by Roth,[2] which also was used successfully in the system $Nb_2O_5-NbO_2F$.[3,4] Two days of heating at 1050°C gave a product consisting of beautiful, rodshaped crystals. X-Ray studies on the crystals showed that the oxide fluoride was isostructural with $NaNb_6O_{15}(OH)$ and the composition was thus concluded to be $NaNb_6O_{15}F$. This was also confirmed by a complete structure determination by one of us (S.A.), which shortly will be published.

In order to learn, whether F^- and OH^- can substitute for each other generally in the systems $AF-Nb_2O_5$ and $AOH-Nb_2O_5$, where A stands for alkali metal, further studies have now been undertaken on the systems $LiF-Nb_2O_5$, $LiNbO_3-Nb_2O_5-H_2O$ and $KNbO_3-Nb_2O_5-H_2O$.

The results for the system $LiF-Nb_2O_5$ will now be reported here.

EXPERIMENTAL

Mixtures of LiF of high purity (Baker's Analyzed, 99.89 %) and α-Nb_2O_5 (Kawecki, 99.99 %) were heated in sealed platinum tubes at temperatures between 800—1200°C. The samples were examined by means of X-ray powder photographs obtained with a Guinier focusing camera of 80 mm diameter, using monochromatized Cu$K\alpha$ radiation. Single crystal photographs were taken with a Weissenberg camera using Cu$K\alpha$ radiation.

The thermal decomposition curve (Fig. 2) was obtained by means of heating a fine-grained sample of the pure compound under a slow stream of dried argon in a horizontal furnace. The sample, kept in a platinum boat, was heated stepwise up to 1310°C. For every observation, marked with a circle in the diagram, the sample was kept at the temperature for an hour and then weighed at room temperature.

RESULTS OF THE PHASE ANALYSIS AND DISCUSSIONS

Samples of the composition $LiF \cdot bNb_2O_5$, where b varied from 1, 2, 3 ... to 14, were heated for two days at temperatures between 1000—1200°C.

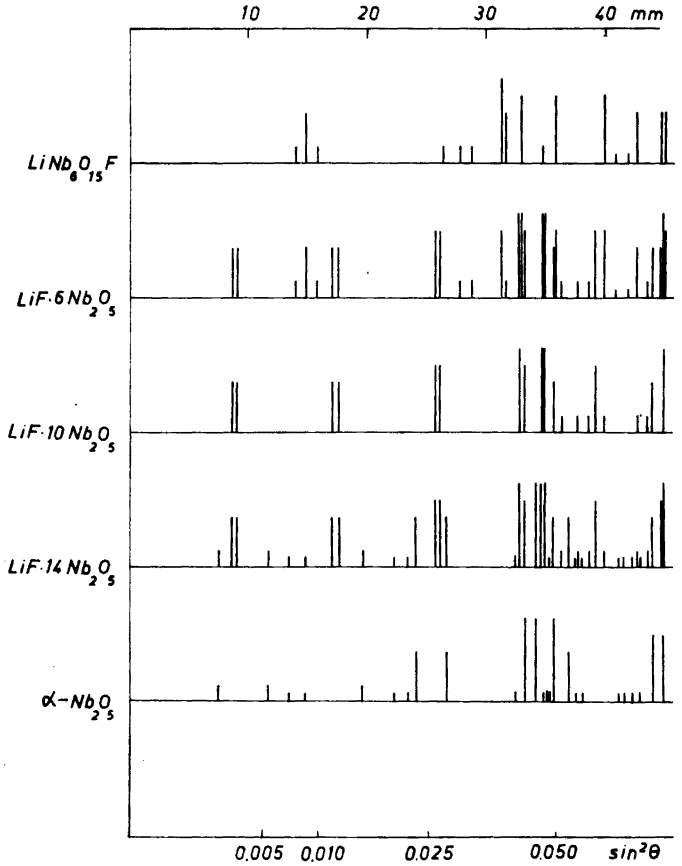


Fig. 1. Powder patterns of some preparations in the system $LiF—Nb_2O_5$.

Samples of the composition $a\mathrm{LiF} \cdot \mathrm{Nb_2O_5}$, where a varied from 1 to 5 were heated between 800—900°C.

For $b = 1$ and 2 very weak lines of LiF could be detected together with a new pattern of lines. For $b = 3$ the lines of LiF had completely disappeared. With $b = 4$ a new set of lines was observed beside those originating from the X-ray powder pattern corresponding to $b = 3$. When b was increased up to 8 the powder lines of $b = 3$ had become very weak and at the composition $b = 10$ a single phase seemed to be present. At $b = 14$ lines from the high temperature form of $\mathrm{Nb_2O_5}$ were clearly visible. The phase analysis is represented in Fig. 1 by means of some X-ray powder patterns.

When a was varied between 2 and 5 at temperatures above 900°C only the two phases LiF and $\mathrm{LiNb_6O_{15}F}$ were identified. Ten days of heat treatment at 850°C showed that beside LiF also $\mathrm{LiNb_3O_8}$ and $\mathrm{Nb_5O_{12}F}$ [3] were present in the samples. Complete reaction at this temperature did not occur. A heavy white vapour was noted when opening the sealed tubes. This is probably due to the hydrolysis of a volatile phase such as $\mathrm{NbOF_3}$ or $\mathrm{NbF_5}$ formed during the heat treatment. The actual composition of this material could not be determined as no further experiments were made. It has, however, been pointed out to one of us (S.A.) by H. Schäfer [5,6] that the formation of crystalline oxide fluorides is due to a transport reaction, in which the two gas molecules $\mathrm{NbOF_3}$ and $\mathrm{NbF_5}$ should be involved.

Table 1. Crystallographic constants for $\mathrm{LiNb_6O_{15}F}$.

Unit cell dimension	a	= 16.64 Å
	b	= 3.96 Å
	c	= 8.89 Å

Systematic absent reflections $h00$ with h odd.
Space group *Pmma* (No. 51) (From the final structure determination) $d_{obs} = 4.62$ $d_{calc} = 4.67$.

Beautiful, colourless and rodshaped crystals up to 0.5 mm in size were formed at the composition $b = 3$. Single crystal X-ray studies showed the crystals to be of orthorhombic symmetry and the crystallographic constants are given in Table 1. The indexed Guinier X-ray powder pattern is given in Table 2. The density calculated for the formula $\mathrm{LiNb_6O_{15}F}$ agreed very well with the observed one (Table 1). The chemical formula $\mathrm{LiNb_6O_{15}F}$ was finally confirmed by means of a complete crystal structure determination performed by one of us (M.L.).[7]

The plate-like crystals of the phase occurring around the composition $\mathrm{LiF} \cdot 10\ \mathrm{Nb_2O_5}$ gave an X-ray powder pattern, which is very similar to that observed for the N-form of $\mathrm{Nb_2O_5}$. The N—$\mathrm{Nb_2O_5}$ was first synthesized by Schäfer [8] with the transport reaction

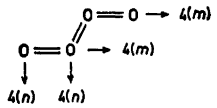
$$\mathrm{Nb_2O_{5(s)}} + 3\ \mathrm{NbCl_{5(g)}} = 5\ \mathrm{NbOCl_{3(g)}}$$

N—$\mathrm{Nb_2O_5}$ has also been obtained under hydrothermal conditions [9] and also during the thermal decomposition of $\mathrm{NbO_2F}$.[10]

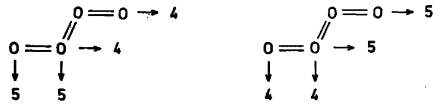
Table 2. Guinier X-ray powder pattern of $LiNb_6O_{15}F$.

I	$\sin^2\Theta_{obs}$	*hkl*	$\sin^2\Theta_{calc}$
w	0.00751	001	0.00751
m	0.00858	200	0.00858
w	0.00969	101	0.00968
w	0.02680	301	0.02680
w	0.03004	002	0.03004
w	0.03217	102	0.03218
vst	0.03775	010	0.03774
w	0.03862	202	0.03862
st	0.04184	401	0.04181
w	0.04631	210	0.04632
st	0.04933	302	0.04934
st	0.06112	501	0.06111
vw	0.06446	311	0.06454
vw	0.06776	012	0.06778
m	0.06972	103	0.06973
m	0.07616	203	0.07617
m	0.07716	600	0.07718
m	0.07955	411	0.07955
w	0.08363	502	0.08364
w	0.08467	601	0.08469
st	0.08709	312	0.08708
m	0.09883	511	0.09885
w	0.10199	412	0.10208
m	0.10731	602	0.10722
st	0.15091	020	0.15096

The essential features of the crystal structure of N—Nb_2O_5 has been derived [9] and the description of it will for the purpose of this paper be limited to a symbolic figure. In a recent paper [11] it was discussed how a group of oxides could be represented by a simple structural formula. The crystal structure of N—Nb_2O_5 belongs according to this notation to the group $B_2C_{m,n}$, where $m = 4$ and $n = 4$. The structure is represented by the following structural symbol



For $n = 5$, $m = 4$ or $n = 4$, $m = 5$ two new hypothetical structures can be derived. They will both have the composition $M_{20}O_{51}$ but differ in their structures, which are shown with the symbols



The powder pattern of the phase found indeed suggests such structural relationships with N—Nb_2O_5. The approximate composition derived, LiF·

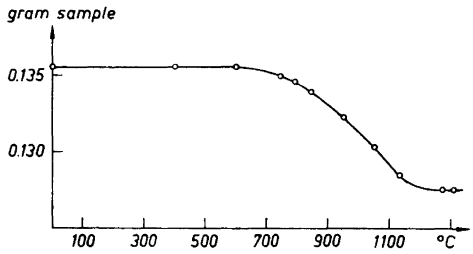


Fig. 2. The gravimetric study of the thermal decomposition of $LiNb_6O_{15}F$.

10-12 Nb_2O_5, agrees also to this. The results of the single crystal studies which have been started on $N-Nb_2O_5$ and $LiF \cdot 10\text{-}12\ Nb_2O_5$, will be reported elsewhere.

The gravimetric study of the thermal decomposition of $LiNb_6O_{15}F$ is demonstrated in Fig. 2. In a separate experiment samples were taken out at 940°C and 1190°C and X-rayed at room temperature. At 940°C considerable amounts of $LiNb_6O_{15}F$ were still present and a small amount of $LiNb_3O_8$ could be detected in the powder pattern. At 1190°C $LiNb_6O_{15}F$ had completely disappeared and the powder pattern showed the $LiNb_3O_8$ phase co-existing with the N-form of Nb_2O_5. At 1310°C, the last point of observation, $N-Nb_2O_5$ had transformed into a-Nb_2O_5. Assuming the fluorine to be transported away by the gas molecule $NbOF_3$, the following formula was derived:

$$3\ LiNb_6O_{15}F = NbOF_3 + 3\ LiNb_3O_8 + 4\ Nb_2O_5$$

The observed loss of weight of 6.1 % is in good agreement with the one calculated for the reaction written above, *viz.* 6.7 %. A reaction involving the formation of NbF_5 would require a loss of weight of 4.6 %.

In order to be able to discuss the mechanism of the very slow decomposition of $LiNb_6O_{15}F$ into the solid phases $LiNb_3O_8$ and Nb_2O_5 a structure determination of $LiNb_3O_8$ has been started.[12]

Acknowledgements. The participation in this work by one of us (M.L.) has taken place within a research program supported by the *Swedish Natural Science Research Council*. For valuable comments on the manuscript we thank Professor Arne Magnéli.

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Received May 7, 1965.