SHORT COMMUNICATIONS

Lithium Aluminum Oxyfluoride Spinel

By Hiroaki YANAGIDA, Goro YAMAGUCHI and Yuzo ONO

Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Tokyo

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Kordes[1] obtained a spinel-like mineral from a mixture of lithium fluoride and aluminum oxide by heating it to 1300°C. He supposed that a $LiF\text{-}Al_2O_3$ spinel form exists. However, he determined the mineral obtained at 1300°C to be $Li_2O\text{-}5Al_2O_3$, which did not contain fluorine; he did not mention the composition of the products at lower temperatures further. All of the spinel structures previously investigated contain only oxygen or sulfur as an anion, except for the aluminum oxynitride spinel, $AlN\text{-}Al_2O_3$, investigated by Yamaguchi and Yanagida[2] and by Adams, AuCoin and Wolff.[3] It may be supposed, from a consideration of the ionic radii, that there exists a spinel form, $LiF\text{-}Al_2O_3$, which contains fluorine as an anion, in comparison with $MgO\text{-}Al_2O_3$ or $AlN\text{-}Al_2O_3$.

TABLE I. DIFFERENCES BETWEEN THE TWO SPINELS

	I $Li_2O\cdot 5Al_2O_3$	II The spinel obtained from $LiF\text{-}Al_2O_3$
Starting materials	Li_2CO_3 + $\gamma\text{-}Al_2O_3\cdot 3H_2O$	LiF 40 mol.%-$\gamma\text{-}Al_2O_3\cdot 3H_2O$
Temp.	>900°C	800—900°C
Lattice dimention	$a=7.906$ Å	$a=7.922$Å
Super lattice peaks		
(2, 1, 1)	12.7	—
(2, 1, 0)	16.5	4.4
(1, 1, 0)	11.6	4.0
F content by NMR	none	present at least 11%

Mixtures of fine-grained $\gamma\text{-}Al_2O_3\text{-}3H_2O$ or $\alpha\text{-}Al_2O_3$ and chemically pure lithium fluoride or lithium carbonate were heated at 600—1200°C for 0.5—3 hr. in an electric furnace in air. The products were then washed with hydrochloric acid to eliminate a trace of contamination by lithium fluoride and were analyzed by powder X-ray diffraction.

The single spinel phase was formed from the mixtures of lithium fluoride (35—40 mol. percent) and $\gamma\text{-}Al_2O_3\text{-}3H_2O$ (60—65 mol. percent) heated at 800—900°C for more than an hour. This spinel phase was then compared with the lithium aluminum oxide spinel, $Li_2O\text{-}5Al_2O_3$ (denoted as I in Table I). The cubic lattice dimensions, the intensity ratios of such super lattice lines[4] as (2, 1, 1), (2, 1, 0), (1, 1, 0) to a normal line (3, 1, 1), are distinctly different in the two spinels. This shows that the II spinel in Table I is to be distinguished from the I spinel.

The semi-quantitative analysis of fluorine was carried out by broad-line NMR using a mixture of AlF_3 and $\alpha\text{-}Al_2O_3$ as a reference. It was ascertained that the II spinel contained more than 11 percent fluorine, which corresponded to about 70 percent of the value calculated from the $LiF\text{-}Al_2O_3$ formula.

Thus, it is suggested that the II spinel obtained in the present work may either be in a spinel formula, $LiF\text{-}(1+x)Al_2O_3$, or in a solid solution of $LiF\text{-}Al_2O_3$ and $Li_2O\text{-}5Al_2O_3$. The true formula will be determined after an exact quantitative analysis of fluorine, which is now being attempted by the present authors using different methods.

1) E. Kordes, *Z. Krist.*, **A91**, 193 (1935).
2) G. Yamaguchi and H. Yanagida, This Bulletin, **32**, 1264 (1959).
3) I. Adams, T. R. AuCoin and G. A. Wolff, *J. Electrochem. Soc.*, **109**, 1050 (1962).
4) P. B. Braun, *Nature*, **27**, 1123 (1952).