On the Refractive Power of the Lower valent Al Ion (Al^{+} or Al^{++}) in the Crystal

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(Received February 19, 1950)

Introduction.—The author found out the spinel crystal with lower valent Al ion in the ingot of abrasive fused alumina, which was made by the special method and its properties were reported in the previous papers.[1] Valency of such Al ion seems mono or di ; mono is more probable because unpaired electron does not exist. This spinel crystal are explained as that two Mg ions of normal spinel ($MgAl_2O_4$) are substituted by Al^{+} ion and Al^{+++} ion (or two Al^{++} ions). The properties of this spinel crystal are as follows;

Color ; coloress

Refractive index ; 1.78

Density ; 3.72

Crystal structure; spinel $a_0=7.97$Å.

Chemical composition (as normal oxide);
Al_2O_3 99.65%, MgO 4.91%, total 104.56%

Probable formula ; (0.412 Al^{+}, 0.412 Al^{+++}, 0.176 Mg) $O \cdot Al_2O_3$

In these values, especially high refractive index of the new spinel crystal are found. This phenomenon would depend on the high polarizability of the lower valent Al ion. In this paper, the calculation of the ionic

1) G. YAMAGUCHI, *J. Electrochem. Assoc. Japan*, **14**, 106 (1946); *J. Ceram. Assoc. Japan*, **55**, 42 (1947).

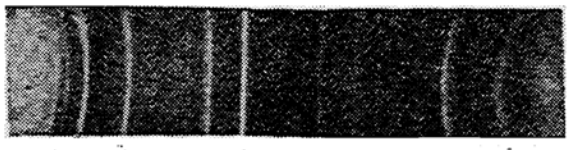

Fig. 1.—X-ray powder photograph of the new spinel crystal by Fe K ray.

refraction of the lower valent Al ion is attempted.

Calculation of the Ionic Refraction of Oxgen Ion in the Normal Spinel Structure.—In this calculation the following values are used ;

Formula weight of spinel, M_{SP}; 142.26
Density of spinel, D_{SP}; 3.578[2]
Refractive index of spinel, N_{SP}^{++}; 1.719[2]
Ionic refraction of Mg^{++}, $R_{Mg^{++}}$; 0.26[3]
Ionic refraction of Al^{+++}, $R_{Al^{+++}}$; 0.17

By introducing these values into Lorentz-Lorentz formula,

$$(N^2 - 1)M/(N^2 + 2)D = R$$

$R_{SP} = 15.69$ is obtained, where R_{SP} is formula refraction of spinel. Now R_{SP} is the sum of $R_{Mg^{++}}$, $2R_{Al^{+++}}$, and $4R_{O^{--}}$, then 3.77 is obtained as the value of ionic refraction of oxgen ion in normal spinel ($R_{O^{--}}$).

Calculation of Ionic Refraction and Ionic Polarizability of Al Ion.—By introducing the refractive index, the formula weight and the density of the new spinel crystal into Lorentz-Lorentz formula, 16.28 is obtained as the value of formula refraction of the new spinel crystal with Al^+ ion. Now 16.28 is the sum of $0.176R_{Mg^{++}}$, $0.412R_{Al^+}$, $2.412R_{Al^{+++}}$ and $4R_{O^{--}}$, then 1.80 is obtaind as the value of R_{Al^+}.

And next, by the equation ;
$\alpha = 3R/4\pi N_O = 0.393 \times 10^{-24}R$, where α is ionic polarizability, 0.727×10^{-24} is obtained as the value of ionic polarizability of Al^+ ion.

These values are ten times as large as that of normal Al^{+++} ion and situated between the values of Ca ion and of Sr ion.

Moreover by the similar calculation in case of Al^{++} ion instead of $(Al^+ + Al^{+++})/2$, 0.98 is obtained as the value of ionic refraction of Al^{++} ion and 0.397×10^{-24}, as the value of ionic polarizability.

Conclusions.—The hypothesis that lower valent Al ion exists as Al^+, is more probable and in such case the following values are obtained ;

Ionic refraction of Al^+; 1.80
Ionic polarizability of Al^+; 0.727×10^{-24},

But if the form of the ion is Al^{++}, the values are as follows ;

Ionic refraction of Al^{++}; 0.98
Ionic polarizability of Al^{++}; 0.397×10^{-24}

The results show the high polarizability of lower valent Al ion depending on loosely combined electron in M shell. Many other particular and interesting properties of the crystal will follow this fact. Now the problem is whether typical Al_3O_4, namely $(0.5Al^+, 0.5Al^{+++})O \cdot Al_2O_3$, exists or not. Perhaps, at normal state, Al^+ ions are not so stable that Al_3O_4 could not able to exist, but if Mg ions are mixed in molten state, spinel structure with Mg ions is stabilized at solidifying time and so Al^+ ions existing in molten state go into spinel structure and stabilized.

A part of the cost of this research has been defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

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2) E. Rinne, *N. Jahb. Min.* (A) **53**, 106 (1928).
3) I. NODA, *J. Electrochem. Assoc. Japan*, **14**, 124 (1946).