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Formation of β-Alumina Type Potassium Gallate and Its Ionic Conductivity

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Mixtures of Ga_2O_3 and K_2CO_3 in the composition range of $Ga_2O_3/K_2O = 4–9$ were sintered at various temperatures. X-ray diffraction patterns showed that the specimens of $Ga_2O_3/K_2O = 4$, 5, and 6 had a β-alumina type structure. $K_2O \cdot 5Ga_2O_3$ sintered at 1500°C belonged to the hexagonal system which was β phase, similar to Na-βAl_2O_3, while that sintered at 1200°C belonged to the rhombohedral system corresponding to the β'' phase, similar to Na-$\beta'' Al_2O_3$. The assignments of indices to their diffraction lines were tried and the crystal structure of the β phase was presumed. The ac conductivities of the β and β'' phases were measured by the use of an impedance bridge, and the ionic transport numbers were examined by a dc polarization technique and Tubandt's electrolysis method. The compounds were revealed to be potassium ion conductors.

1. Introduction

The electrolytes for solid-state batteries which exhibit high power and energy densities are required to have high ionic and extremely low electronic conductivities. These electrolytes are classified as "super ionic conductors." One of the most familiar super ionic conductors is β-alumina which is a sodium ion conductor and has been used as the electrolyte for sodium–sulfur batteries (*1*). It has an ideal formula of $NaAl_{11}O_{17}$ or $Na_2O \cdot 11Al_2O_3$. Two stable phases have been reported in the $Na_2O–Al_2O_3$ system: one is hexagonal β phase (Na-βAl_2O_3) and the other is rhombohedral β'' phase (Na-$\beta'' Al_2O_3$) (*1*), which is ideally represented by $Na_2O \cdot 5Al_2O_3$.

β- and β''-alumina type phases have also been known in systems such as $K_2O–Al_2O_3$ (*2*), $K_2O–Fe_2O_3$ (*2–4*), and $Na_2O–Ga_2O_3$ (*5*). Recently, the formation region of β-alumina type potassium ferrite (K-βFe_2O_3) was examined, and the phase diagram of the $KFeO_2–Fe_2O_3$ system was proposed (*4*). β phase was found in the region of $Fe_2O_3/K_2O = 6–6.8$ at temperatures higher than 1150°C and the mixture of β and β'' phases was shown at lower temperature. In the $Na_2O–Ga_2O_3$ system, the fields of existence of β and β'' phases were determined crystallographically and the ionic conductivity of the β phase was measured by Boilot (*5*).

Only β phase has been shown in the $K_2O–Ga_2O_3$ system, but its formula has not yet been determined. The reported formulas are $K_2O \cdot 11Ga_2O_3$ (*6*), $K_2O \cdot 6Ga_2O_3$ (*7*), and $K_2O \cdot 5Ga_2O_3$ (*8*). Furthermore, the electrical conduction data of β-alumina type potassium gallate have scarcely been obtained (*9*).

In this paper, the formation of a β-alumina type compound in the $K_2O–Ga_2O_3$ system is investigated and its ionic conduction is examined.

2. Experimental

2.1. Sample Preparation

K_2CO_3 and βGa_2O_3 were used as starting materials. The examined composition ratios of Ga_2O_3 to K_2O ranged from 4 to 9. Mixing was accomplished by grinding the weighed powders in an agate mortar using ethanol as dispersing reagent. Subsequently, the alcohol was removed by drying at 100°C.

The powder was pressed to form a tablet in a die at about 1 kbar pressure and was prefired at 900°C for 24 hr in air. The sample was ground again in ethanol. After removal of the alcohol, the prefired powder was isostatically pressed under a pressure of about 3 kbar. The tablet was then sintered at various temperatures for 1–20 hr in air. The very small weight change of the tablet suggested the evaporation of some alkali oxide during the sintering process, but the chemical analysis failed to detect any deviation of the composition from the original ratio of gallium to alkali.

The tablet thus obtained was reground to prepare the fine powder (325 mesh pass) for X-ray diffraction, which was carried out by using a copper target, a nickel filter, and a scintillation counter. The diffraction pattern was obtained by ordinary goniometer scanning speed ($2° \cdot 2\theta$/min) and moderate chart speed (2 cm/min). In the case of measurement of lattice parameters these speeds were lowered to $1/4° \cdot 2\theta$/min and 1 cm/min, respectively, and the silicon powder was used as an inner standard material.

2.2. Conductivity Measurement

The total conductivities of the sintered samples were measured over a temperature range from 200 to 500°C in air. The surface of the tablet was polished using emery paper of 800–1200 #, and a specimen about 8 mm in diameter and about 2 mm thick was prepared. The specimen was sandwiched between two electrodes of gold foil and was pressed down by stainless-steel plates with a spring. The impedance versus frequency plot flattened out at frequencies higher than about 10 kHz, so the values taken at 10 kHz were adopted as resistance.

The dc polarization curves, shown in Fig. 1, showed whether the conduction was ionic or electronic (*10*). The sample was sandwiched between two blocking electrodes of gold plate. A direct current with a time interval of a few minutes was passed under the condition of an applied voltage lower than the decomposition voltage of the sample. If the curve is of type a in Fig. 1, the conduction can be judged to be a mixture of ionic and electronic, and the ionic part is approximated by the equation, $t_i = (V_s - V_i)/V_s = V_r/V_s$. On the other hand, if the curve is of type b, the conduction will be chiefly ionic.

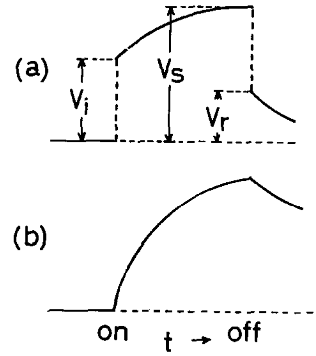

FIG. 1. Typical dc polarization curves. (a) Voltage–time curve, where V_i is initial voltage, V_s is steady-state voltage, and V_r is the residual voltage. (b) Voltage–time curve, indicating that ionic conduction is predominant.

In order to determine the mobile species and ionic conductivities, the transport numbers of various specimens were measured at 300 and 500°C by Tubandt's electrolysis method. Sample arrangements are shown schematically in Figs. 2a and b, where a has three of the same specimens and b has one specimen and two electrodes of K-βFe$_2$O$_3$ (*4*). In both cases, the current collector was gold plate on silver wire.

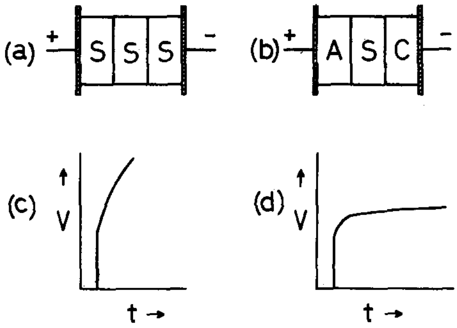

FIG. 2. Model of electrolysis. (a), (b) Arrangement of samples, where *S* is specimen, and *A* and *C* are K-βFe$_2$O$_3$ as electrodes. (c), (d) Voltage–time curves corresponding to (a) and (b), respectively.

3. Results

3.1. *X-Ray Diffraction*

The samples with the composition of $Ga_2O_3/K_2O = 4$, 5, and 6 showed an X-ray diffraction pattern analogous to that of Na-βAl_2O_3 and the samples of $Ga_2O_3/K_2O =$ 7, 8, and 9 showed mixed patterns of the β-alumina type and gallium oxide phases. The following descriptions are restricted to the results of the composition of $K_2O \cdot 5Ga_2O_3$ with the typical single phase. The samples sintered at 1200 and 1500°C showed fairly similar patterns, but careful observations find several differences between them.

TABLE I

Diffraction Indices of Specimen Sintered at 1500°C for 1 hr in Air after Prefiring at 900°C for 24 hr (System is Hexagonal, $a = 5.835$ Å, $c = 23.50$ Å)

Number	$h\,k\,l$	$d_{calc.}$	$d_{obs.}$
1	0 0 2	11.75	11.7
2	0 0 4	5.875	5.87
3	0 1 2	4.642	4.65
4	0 1 3	4.246	4.25
5	0 1 6	3.096	3.09
6	1 1 0	2.917	2.92
7	0 1 7	2.796	2.79
8	1 1 4	2.613	2.62
9	0 2 1	2.512	2.51
10	0 2 2	2.470	2.48
11	0 2 3	2.405	2.41
12	1 1 6	2.340	2.34
13	0 2 4	2.321	2.32
14	0 2 5	2.225	2.23
15	0 2 6	2.123	2.13
16	0 2 7	2.019	2.02
17	0 2 , 10	1.721	1.72
18	0 3 0	1.684	1.68
19	0 0 , 14	1.679	1.68
20	1 2 7	1.660	1.66
21	0 2 , 11	1.631	1.63
22	0 3 4	1.619	1.62
23	1 2 8	1.601	1.60
24	0 3 6	1.547	1.55
25	1 2 , 10	1.482	1.48
26	0 2 , 13	1.470	1.47
27	2 2 0	1.459	1.46
28	2 2 2	1.448	1.45
29	2 2 4	1.416	1.42
30	0 2 , 14	1.398	1.40

TABLE II

Diffraction Indices of Specimen Sintered at 1200°C for 5 hr in Air after Prefiring at 900°C for 24 hr (System is Hexagonal (Rhombohedral), $a = 5.832$ Å, $c = 35.61$ Å)

Number	$h\,k\,l$	$d_{calc.}$	$d_{obs.}$	d (by Hoffman)
1	0 0 3	11.870	11.8	11.8
2	0 0 6	5.935	5.90	5.90
3	0 1 2	4.859	4.86	4.86
4	1 0 4	4.393	4.40	4.40
5	1 1 0	2.916	2.91	2.92
6	0 1 , 11	2.725	2.71	2.71
7	1 1 6	2.617	2.62	2.61
8	0 2 1	2.519	2.52	2.52
9	0 2 4	2.429	2.43	2.43
10	0 0 , 15	2.374	2.38	—
11	1 1 9	2.347	2.34	2.34
12	0 2 7	2.262	2.26	2.25
13	0 2 , 10	2.060	2.06	
14	0 1 , 20	1.679	1.68	
15	0 2 , 16	1.670	1.67	
16	1 2 , 11	1.644	1.64	
17	2 0 , 17	1.612	1.61	
18	0 3 9	1.549	1.55	
19	2 2 0	1.458	1.46	
20	2 2 6	1.416	1.42	
21	0 2 , 22	1.363	1.36	

On the basis of these observations, the indices were assigned to the diffraction lines. Table I showed the indices together with the observed spacings. The good agreement between the calculated and the observed spacings seems to prove the assigned indices to be suitable. This indicates that the high temperature modification of potassium gallate is β phase, analogous to Na-βAl_2O_3. Assignment of the same indices as shown in Table I was tried for the pattern of the sample obtained by sintering at 1200°C, but the trial failed in agreement between the calculated and observed spacings. This suggested that the low temperature modification of the sample differed from β phase. Then, another assignment with the assumption of rhombohedral symmetry was made. Table II shows the indices converted to hexagonal symmetry except for the lines of very weak intensity. Both the calculated and the observed spacings showed fairly good agreement with each other, and the latter also agreed with the data of Hoffman (*8*). These results reveal that the low temperature modification of potassium gallate is β'' phase, similar to Na-$\beta''Al_2O_3$, and that Hoffman's data on $K_2O \cdot 5Ga_2O_3$ are concerned with the rhombohedral phase.

3.2. Ionic Conductivity

The temperature dependence of total conductivity is shown in Fig. 3. The conductivity curves are approximately linear and the equation $\sigma = A \cdot \exp(-E/RT)$ is applied, where A is constant, E is the apparent activation energy for conduction, and R is the gas constant. The E values calculated from the slopes of curves a, b, and c are 40.9, 39.5, and 37.1 kJ/mole, respectively. The conductivity of the sample sintered at 1400°C was almost the same as that of the sample sintered at 1500°C.

The polarization curve was of the same type as Fig. 1b in the temperature range 250–500°C, which suggested that the conduction in the samples was chiefly ionic. The electrolysis method was applied to examine the conduction in detail. When the specimen arrangement was a type a in Fig. 2, the voltage–time curve was shown in c and the voltage increased up to the limiting value (about 13 V) of the current generator used in a few minutes. Under this arrangement a low current and long-term electrolysis would be needed to obtain a measurable weight change of specimen.

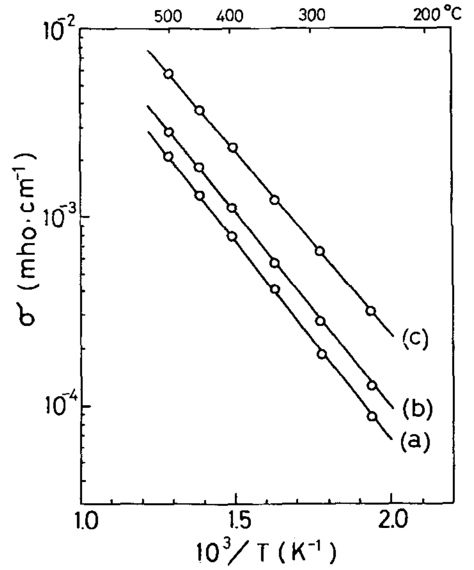

FIG. 3. Total conductivities of $K_2O \cdot 5Ga_2O_3$ sintered at 1200°C (a), 1300°C (b), and 1500°C (c).

TABLE III

WEIGHT CHANGES OF THE TABLETS AFTER ELECTROLYSIS[a]

Tablet	ΔW (mg) Observed	ΔW (mg) Calculated	$\Delta W_{obs.}/\Delta W_{calc.}$
A	−11.0	−10.9	1.0_0
B	0	0	—
C	+13.0	+10.9	1.1_9

[a] Amount of electricity was 27.0 C. Tablets A and C are K-βFe_2O_3 and B is the specimen.

Another arrangement shown in Fig. 2b showed a *V–t* curve like Fig. 2d. In this case, high current, e.g., 500 μA, could be passed for a long time and adequate weight change could be observed. Table III shows one of the weight changes of the specimens together with the calculated values, assuming that only the potassium ion is a mobile species. The observed values were in good agreement with the calculated values, especially in the case of tablet A. If the gallium ion is the chief charge carrier, a weight change of 6.50 mg should be observed. Furthermore, on the assumption that the charge carrier is the oxygen ion, the weight change should be 2.24 mg. The transport number of the potassium ion from these data was considered to be 1.0. Therefore, the conductivities shown in Fig. 3 directly indicated the potassium ion conductivities.

4. Discussion

4.1. Formation of β-Alumina Type Potassium Gallate

X-ray diffraction studies indicated that Ga_2O_3 reacted with K_2O to form a β-alumina type compound. βGa_2O_3 has a deformed spinel type or γAl_2O_3-like structure, in analogy with γFe_2O_3, and αGa_2O_3 shows a trigonal structure, similar to αAl_2O_3 and αFe_2O_3. It is considered to be reasonable from the profile that the obtained compound has the same structure as Na-βAl_2O_3 or Na-$\beta'' Al_2O_3$. The radii of Al^{3+}, Fe^{3+}, and Ga^{3+} are 0.51, 0.64, and 0.62 Å, respectively. Tables IV and V show a comparison of lattice parameters of some β and β'' phases. It can be seen from these tables that the lattice parameter increases with the increase of the radius of trivalent metal ion. In addition, β phase appears to have a wide range of alkali content. X-ray diffraction showed another characteristic: The

TABLE IV

COMPARISON OF LATTICE PARAMETERS OF SOME COMPOUNDS WITH β-ALUMINA TYPE PHASE

Phase		Lattice parameters (Å)				
		Dyson and Johnson (*2*)	Roth and Romanczuk (*3*)	Ohtsubo and Yamaguchi (*11*)	Scholder Mansmann (*7*)	Takahashi *et al.* (*4*)
$K_2O\cdot 11Al_2O_3$	*a*	5.595			5.584	
	c	22.71			22.67	
$K_2O\cdot 11Fe_2O_3$	*a*	5.916			5.915	
	c	23.79			23.68	
$K_2O\cdot 7 \sim 6\ Fe_2O_3$	*a*		5.929	5.932		5.934
	c		23.80	23.74		23.94
$K_2O\cdot 11Ga_2O_3$	*a*				5.80	
	c				23.5	
$K_2O\cdot 5Ga_2O_3$	*a*					5.835[a]
	c					23.50

[a] This work.

TABLE V

COMPARISON OF LATTICE PARAMETERS OF SOME COMPOUNDS WITH β''-ALUMINA TYPE PHASE

Phase		Lattice parameters (Å)				
		Yamaguchi and Suzuki (*12*)	Dyson and Johnson (*2*)	Roth and Romanczuk (*3*)	Rooymans *et al.* (*13*)	Takahashi *et al.* (*4*)
$K_2O\cdot 6Al_2O_3$	*a*	5.595	5.603			
	c	34.226	34.04			
$K_2O\cdot 7Fe_2O_3$	*a*			5.927		
	c			35.88		
$K_2O\cdot 5Fe_2O_3$	*a*				5.933	
	c				35.865	
$K_2O\cdot 5Ga_2O_3$	*a*					5.832[a]
	c					35.61

[a] This work.

samples with compositions of $Ga_2O_3/K_2O = 4$, 5, and 6 had almost the same pattern. This indicated the nonstoichiometry of both β and β'' potassium gallate in analogy with sodium gallate (*5*).

It is interesting to consider what kind of packing β-alumina type potassium gallate shows. The analogous composition of β''-potassium gallate (K-$\beta''Ga_2O_3$) and β''-sodium aluminate (Na-$\beta''Al_2O_3$) suggests they have the same packing. On the other hand, two types of structures of β phase potassium gallate (K-βGa_2O_3) are proposed in this paper, assuming the composition $K_2O \cdot 5Ga_2O_3$ or $K_2Ga_{10}O_{16}$.

The first structure is based on the assumption that the same number of oxygen ions is contained in a unit cell as in ideal Na-βAl_2O_3 ($Na_2Al_{22}O_{34}$), and its formula must be $K_{4.25}Ga_{21.25}O_{34}$. This compound consists of two parts, that is, the so-called K–O layer and the spinel-like block, and the formula will be rewritten as ($K_{4.25}Ga_{3.25}O_2$) ($Ga_{18}O_{32}$). A comparison of this with the ideal formula ($K_2Ga_4O_2$) ($Ga_{18}O_{32}$) indicates a reduction of the number of gallium ions from 4 to 3.25, leaving the gallium ion vacancy statistically in the K–O layer. Thus, the increased concentration of potassium ions which occupy the mid-oxygen (*m*O) sites in the mirror plane is accompanied by a shift of potassium ions from the *BR* site to the *m*O site, as reported by Peters (*14*).

The second structure assumes the same number of gallium ions in a unit cell as that of aluminium ion in ideal $Na_2Al_{22}O_{34}$. In this case the $K_{4.40}Ga_{22}O_{35.20}$ is rewritten as ($K_2Ga_4O_2 \cdot 1.20K_2O$)($Ga_{18}O_{32}$), which indicates the formation of a solid solution between ($K_2Ga_4O_2$)($Ga_{18}O_{32}$) and $1.20K_2O$ in the following manner. Excess potassium ions occupy the *m*O sites, while one excess oxygen ion statistically enters the remaining space in the K–O layer. This structure allows K_2O to enter the mirror plane over a range of x in the formula ($K_2Ga_4O_2 \cdot xK_2O$) ($Ga_{18}O_{32}$). In practice, X-ray diffraction indicated that x took the values of 1.75–0.83, corresponding to $Ga_2O_3/K_2O = 4$, 5, and 6. From these results, the present authors lean toward this second structure.

4.2. *Potassium Ion Conduction*

The dc polarization curves suggested that the chief conduction is ionic. The observed weight change in tablet A (shown in Table III) agreed well with the calculated one, but that in tablet C was somewhat greater than the calculated value. Such a discrepancy was usually observed in the cathode side tablet, and on the surface contacting the gold plate yellowish reaction products were found. This product indicated basicity to litmus and was so hygroscopic that tablet C took up primarily water and secondarily carbon dioxide during weighing, which produced the discrepancy mentioned above. These results bore out the potassium ion transport through tablet B from anode to cathode and confirmed potassium gallate as a potassium ion conductor. In electrolysis, K-βFe_2O_3 will play the part of a reversible electrode for potassium ion, similarly to sodium tungsten bronze for sodium ion (*15*).

It was interesting to compare the conductivity obtained by Boilot for β-alumina type sodium gallate (Na-βGa_2O_3) with that obtained in this work for potassium gallate (K-βGa_2O_3). The conductivity of Na-βGa_2O_3 at 300°C is 3×10^{-2} mho·cm^{-1}, which is one order of magnitude higher than that of K-βGa_2O_3. Such a relation is also seen in sodium and potassium β-aluminas. The self-diffusion coefficient of sodium ion in single-crystal Na-βAl_2O_3 at 300°C is about 10^{-5} cm^2/sec, whereas that of potassium ion is about 10^{-6} cm^2/sec (*16*). Furthermore, the conductivity of the sodium ion in polycrystalline Na-βAl_2O_3 is about 10^{-2} mho·cm^{-1} and that of potassium ion in K-βAl_2O_3 is about 10^{-3} mho·cm^{-1} (*9*).

The apparent activation energy for potassium ion conduction of K-βGa_2O_3 was 37.1 kJ/mole which was somewhat larger than that of K-βAl_2O_3. The value reported was 25.9 kJ/mole in K-βAl_2O_3 (*9*). On the other hand, the value for sodium ion conduction was given as 19.2 kJ/mole in Na-βAl_2O_3 (*9*) and 26.3 kJ/mole in Na-βGa_2O_3 (*5*).

In sodium aluminate and gallate, the conductivity was higher than that of potassium aluminate and gallate, while the apparent activation energy for conduction of the former was lower than that of the latter. These values seem to relate mainly to the ionic radii of sodium and potassium. In other words, it appeared that they relate to the ionic mobilities the magnitudes of conduction paths such as the slot width, or the conduction mechanisms. More extensive X-ray and electrochemical study on single crystals would be required to discuss these problems.

5. Summary

The formation of β-alumina type compound in the K_2O–Ga_2O_3 system was investigated and its ionic conduction was examined. The specimen sintered at 1500°C had hexagonal symmetry (β phase) and the one sintered at 1200°C had rhombohedral system (β'' phase). The potassium ion conductivity of the β-phase at 300°C was about 10^{-3} mho·cm^{-1} and the apparent activation energy for potassium ion conduction was about 37 kJ/mole.

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