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Potassium ion conduction in the β-alumina type compound $K_2O\cdot(5\text{-}x)Ga_2O_3\cdot xFe_2O_3$

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The sintered materials $K_2O\cdot(5-x)Ga_2O_3\cdot xFe_2O_3$, which were found to have β-alumina type structures in the range of $0 \leqslant x \leqslant 5$, showed mixed ionic and electronic conduction. The potassium ion conductivity estimated from the total conductivity and the transport number increased as the gallium was replaced by iron; the apparent activation energy for potassium ion conduction decreased slightly with the iron content. The phenomenon was explained in terms of the expansion of the structural slot.

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1. Introduction

Recently, the formation of β-alumina type potassium gallate in the system K_2O–Ga_2O_3 and its ionic conduction were investigated by the present authors [1]. The specimen with the composition of $K_2O\cdot 5Ga_2O_3$ sintered at 1500° C showed a β phase of hexagonal symmetry similar to Na-β-Al_2O_3, whereas when it was sintered at 1200° C it had a β″ phase of rhombohedral system similar to Na-β″–Al_2O_3. The potassium ion conductivity of the β-phase was about 10^{-3} $(\Omega\,\text{cm})^{-1}$ at 300° C and the apparent activation energy for potassium ion conduction was about 37 kJ mol^{-1}.

The present authors also studied the gallate in which gallium was substituted with aluminum to form the compound $K_2O\cdot(5-x)Ga_2O_3\cdot xAl_2O_3$ [2]. This potassium gallate was a potassium ion conductor and the potassium ion conductivity decreased with the amount of alumina. The decrease of the ionic conductivity was explained by the decrease of the slot width.

From the investigation on the hydrostatic pressure dependence of the ionic conductivity of β-alumina analogs [3], it may be expected that the increase of the slot width in the potassium gallate will result in an increase of the potassium ion conductivity. In this work, the homogeneous range of substitution for gallium with iron (which is larger than gallium) is examined together with the effect of the substitution on the expansion of the slot width.

2. Experimental

2.1. *Preparation of the sample*

The starting materials were K_2CO_3, βGa_2O_3 and αFe_2O_3. Both K_2CO_3 and βGa_2O_3 were reagent grade, and αFe_2O_3 was obtained by the thermal decomposition of ferrous oxalate at 600° C for 10 h in air. The sample was prepared according to the formula $K_2O\cdot(5-x)Ga_2O_3\cdot xFe_2O_3$ in the range of $0 \leqslant x \leqslant 5$. The mixed and dried powder was pressed to form a tablet at about 1 kbar and the tablet was fired at 950° C for 24 h. The sample was ground in ethanol, and after removal of the alcohol the prefired powder was isostatically pressed in a rubber balloon at about 3 kbar. The tablet was sintered at 1500° C for 1 h in air and its surface was polished by emery paper to form the specimen (8 mm in diameter and 2 mm thick) which was used for X-ray diffraction and electrical measurements.

2.2. *X-ray diffraction*

The tablet was ground to produce a powder as fine as 325 mesh for X-ray diffraction. The diagrams were taken at room temperature using a cobalt target and scintillation counter. The lattice parameters were measured with the aid of the (017) and (114) diffraction lines.

2.3. *Conductivity measurement*

The total conductivity of the sintered specimen was measured in the temperature range from 200 to 500° C in air. The frequency dependence of the conductivity decreased as the iron content became larger. Because the conductivity did not increase at frequencies higher than 10 kHz, it was measured at 10 kHz.

In order to determine the conducting species, the d.c. polarization technique was applied. This was described in more detail in the previous paper [1]. The ion transport number was measured by the use of the electrolysis method [1].

3. Results

3.1. *Potassium gallate derivatives*

The degree of sintering or apparent porosity was estimated from the density of the fired sample. The apparent density of the sample is shown in Fig. 1. The density decreases monotonically with the increase of substitution, which does not immediately mean a lowering of the degree of sintering. This phenomenon also arises from the difference of the atomic weights of gallium and iron. The apparent porosity was calculated using the equation $P = (1 - \rho_0/\rho_c) \times 100$ (%), where ρ_0 is the apparent density and ρ_c represents the density calculated on the basis of the ideal potassium gallate $K_2O \cdot 11Ga_2O_3$. The P value obtained was less than 10% over the whole composition range.

X-ray diffraction showed the patterns corresponding to the β-alumina type structure at all compositions. The successive shifts of the individual diffraction lines towards the lower angle side suggested an increase of the lattice parameters. Fig. 2 indicates the lattice parameters of the samples. Both *a* and *c* follow monotonically ascending curves and the rate of increase in *c* is larger than that of *a*. The parameters of the sample in which all gallium was replaced by iron are 5·93 Å for *a* and 23·91 Å for *c*. These agreed fairly well with the values for β-alumina type potassium ferrite [4].

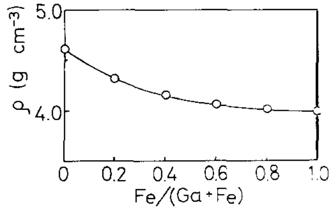

Fig. 1. Apparent density of the potassium gallate substituted by ferrite, $K_2O \cdot (5 - x)Ga_2O_3 \cdot xFe_2O_3$.

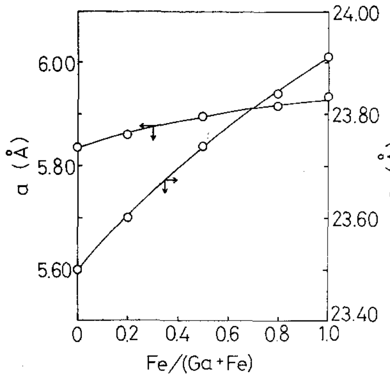

Fig. 2. Lattice parameters of β-alumina type potassium gallate derivatives.

3.2. *Conductivity*

The total conductivities are indicated in Fig. 3. The conductivity increases remarkably and the slope becomes smaller with increasing iron content.

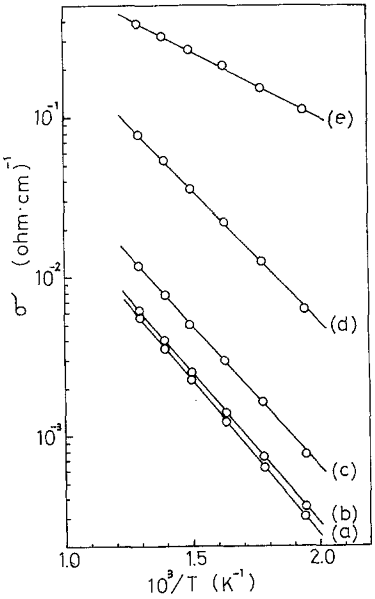

Fig. 3. Total conductivities of the samples with the composition Fe/(Ga + Fe) of (a) 0, (b) 0·2, (c) 0·4, (d) 0·6, and (e) 0·8.

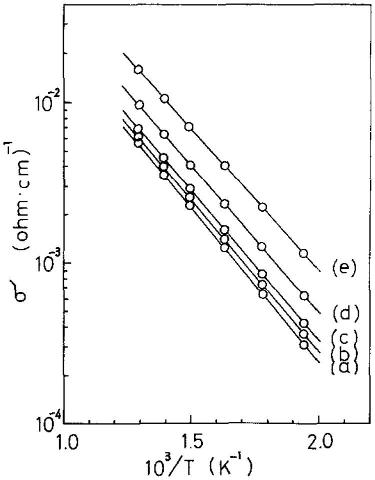

Fig. 4. Potassium ion conductivities of the gallate derivatives with the iron content Fe/(Ga + Fe) of (a) 0, (b) 0·2, (c) 0·4, (d) 0·6 and (e) 0·8.

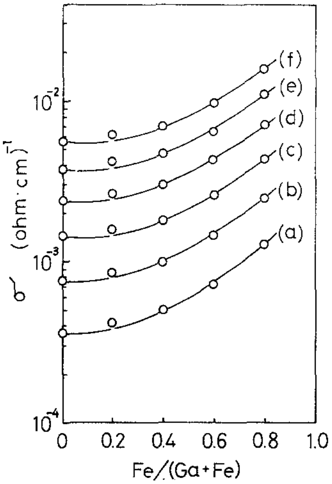

Fig. 5. Conductivity isotherm of potassium ion. Temperatures are (a) 250, (b) 300, (c) 350, (d) 400, (e) 450 and (f) 500° C.

These changes would not, however, directly correspond to the changes of the potassium ion conductivities. It is necessary to separate the electronic conductivity accompanied by iron-substitution from the total conductivity.

The profile of the voltage–time curve in a d.c. polarization experiment indicated that the conduction in the potassium gallate derivatives is mixed ionic and electronic. In order to get more quantitative information on the conduction, the samples were electrolysed at various temperatures. The weight changes of the tablets by the electrolysis are listed in Table 1 along with those calculated on the assumption that the chief carrier is the

Table 1. The weight changes of the tablets $K_2O\cdot(5-x)Ga_2O_3\cdot xFe_2O_3$ by the electrolysis at 350° C

Fe/(Ga + Fe)	*Amount of electricity* (C)	*Tablet**	ΔW (mg) *observed*	ΔW (mg) *calculated*	$\Delta W_{obs}/\Delta W_{calc}$
		A	− 11·0	− 10·9	
0	27·0	S	0	0	1·0
		C	+ 13·0	+ 10·9	
		A	− 8·2	− 8·46	
0·2	20·9	S	0	0	0·99
		C	+ 8·6	+ 8·46	
		A	− 12·2	− 23·0	
0·4	56·7	S	0	0	0·54
		C	+ 12·6	23·0	
		A	− 10·5	− 87·0	
0·6	215	S	0	0	0·11
		C	+ 12·2	+ 87·0	
		A	− 9·4	− 496	
0·8	1224	S	0	0	0·02
		C	+ 10·6	+ 496	
		A	− 8·6	− 600	
1·0	1490	S	0	0	0·01
		C	+ 9·1	+ 600	

* Tablets A and C are K-Fe_2O_3 [4] and S is the specimen.

potassium ion. The ratio of these values is regarded approximately as the potassium ion transport number. From this table, the potassium gallate seems to change from a potassium ion conductor to an electronic conductor with increasing the replacement.

Fig. 4 shows the potassium ion conductivity estimated from the total conductivity and the ratio of the weight change in the electrolysis experiment. The slope of the curves shows a small decrease with increasing ratio of substitution. The apparent activation energies for potassium ion conduction calculated from the slopes are 37·1 kJ mol^{-1} for the sample of Fe/(Ga + Fe) = 0 and 33·7 kJ mol^{-1} for that of Fe/(Ga + Fe) = 0·8.

The isotherms of the ionic conductivities are plotted in Fig. 5. The conductivity increases gradually as the substitution proceeds.

4. Discussion

4.1. *Homogeneous phase*

X-ray diffraction analysis of the potassium gallate derivatives shows a systematic change of the diffraction intensities and in addition the lattice parameters of the samples indicate the uniform increasing curves with the variation of the iron content (Fig. 2). These results suggest that the substitution for gallium with iron is achieved homogeneously. The homogeneous phase in the iron-substituted gallates extends from the substitution ratio of 0 to 1·0, while that in the aluminium-substituted gallates ranges only from the ratio of 0 to 0·5 [2]. This difference of homogeneity between the K_2O–Ga_2O_3–Fe_2O_3 and K_2O–Ga_2O_3–Al_2O_3 systems will be related to the ionic radii of the trivalent cations. The radius of Ga^{3+} (0·62 Å) is nearer to that of Fe^{3+} (0·64 Å) than to Al^{3+} (0·51 Å). Furthermore, the fact that the variation of the lattice parameters with substitution is smaller in the former system than in the latter may well be explained by the size of the trivalent cation. The more similar the radius of the trivalent ions, the wider is the homogeneous range and the smaller is the difference in the lattice parameter. It is reasonable that the principle, 'the more similar, the more soluble with each other' is applied to the behaviour in substitution.

4.2. *Ionic conduction*

In the case of the gallate substitution by aluminate [2], the potassium ion conductivity decreases with increased replacement and the decreasing behaviour was well explained by the apparent porosity and the decrease of the structural slot width with the aluminium-substitution. The potassium gallate derivatives substituted by iron have, however, almost the same porosities at all compositions. Therefore, the discussion on the ionic conduction is confined to the slot width to simplfy the argument.

The slot width was estimated in the same manner as in the case of aluminium-substitution. The β-alumina type structure contains the 'spinel-like' block approximated by a cubic close packing of the oxygen ions. The lattice of the potassium gallate derivative was assumed to expand isotropically in the spinel-like block. The slot width, W, was obtained using the following equation:

$$W = c/2 - \{(22{\cdot}49/2 - 4{\cdot}76) + (a - 5{\cdot}59)\}$$

where 22·49 and 5·59 are the lattice constants and 4·76 is the slot width of Na-βAl_2O_3 [5], and a and c are the lattice parameters of the sample. The second term in the right-hand side of the equation stands for the length of the spinel-like block along the c direction.

Fig. 6 shows the slot width plotted against the iron content. It is concluded [3] that the increase of the slot width leads to the increase of the monovalent cation conduction. The conductivity isotherms shown in Fig. 5 correspond well to this picture. A small decrease in the apparent activation energy for potassium ion conduction may also correspond to an increase of the slot width. In other words, the expansion of the slot leads to an increase in the mobility of the potassium ion.

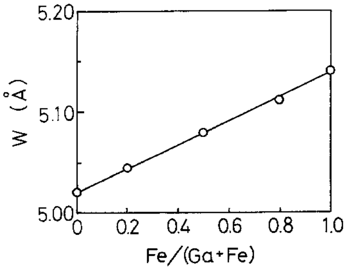

Fig. 6. Slot width calculated from the lattice parameters assuming the isotropic expansion of the spinel-like block.

The facts show that the substitution of gallium ion by a larger ion such as iron has the same effect on the ionic conduction as the hydrostatic pressure.

It is difficult to discuss precisely the ionic conduction of polycrystalline solids, since mass transfer along grain boundaries and along the surface as well as through the bulk may contribute to the conduction. Strictly speaking, the ionic conduction should be discussed on the basis of data obtained using single crystals and an electrode reversible to the mobile ion.

5. Summary

The potassium gallate derivatives $K_2O \cdot (5-x)Ga_2O_3 \cdot xFe_2O_3$ fired at 1500° C were found to have a homogeneous phase of β-alumina type in the range of $0 \leqslant x \leqslant 5$. The gallate was shown to vary from a potassium ion conductor to an electronic conductor with increasing substitution of gallium with iron. The conductivity isotherm of the potassium ion increased gradually with the ratio of the substitution; it was discussed on the basis of the expansion of the structural slot width.

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