h	k	l	d_{obs}	d_{cal}	$2\theta(\text{CuK}\alpha)$ (deg.)	I_{obs}
4	2	2		1.6329		vw
0	2	3	1.6032	1.6036	57.430	vw
8	0	4	1.5997	1.5993	57.565	vw
2	2	3	1.5989	1.5990	57.600	vw
9	1	1	1.5755	1.5756	58.535	vw
7	1	4	1.5688	1.5683	58.810	vw
10	0	1	1.5640	1.5588	59.010	vw
9	1	0		1.5569		vw
4	2	2	1.5532	1.5536	59.460	vw
9	1	2	1.5468	1.5468	59.730	vw
2	2	3	1.5433	1.5420	59.880	vw
10	0	0	1.5374	1.5363	60.135	vw
10	0	2	1.5357	1.5354	60.205	vw
4	0	5	1.5309	1.5307	60.415	vw
4	2	3	1.5298	1.5294	60.465	vw
2	0	6	1.5180	1.5183	60.985	vw
7	1	3	1.5073	1.5075	61.465	vw
0	0	6	1.4964	1.4969	61.960	vw
9	1	1		1.4957		vw
4	0	6	1.4828	1.4822	62.590	vw
10	0	1	1.4733	1.4734	63.040	vw
10	0	3	1.4720	1.4718	63.105	vw
0	2	4		1.4499		vw
4	2	3		1.4342		vw
2	0	6	1.4237	1.4247	65.505	vw
4	2	4	1.4084	1.4083	66.310	vw
9	1	2		1.4054		vw
6	2	2	1.4015	1.4018	66.680	w
8	2	1		1.3593		vw
8	2	0	1.3507	1.3503	69.540	vw
8	2	2	1.3376	1.3377	70.320	vw
11	1	2	1.3161	1.3158	71.645	w
8	2	1	1.3125	1.3125	71.865	vw
11	1	0		1.3108		vw
12	0	2		1.2901		vw
4	2	5	1.2845	1.2847	73.690	vw
10	0	5	1.2796	1.2794	74.015	vw
12	0	1	1.2345	1.2385	76.915	vw
6	0	7	1.2338	1.2338	77.260	vw

3	3	0		1.2290		vw
3	1	7	1.2281	1.2278	77.690	vw
3	3	1	1.2242	1.2243	77.985	vw
1	3	2		1.2191		vw
3	3	1	1.2104	1.2110	79.040	vw
1	3	2		1.2103		

and the powder data are listed in Table 3.

4. Summary

Crystals of potassium hexa-titanate are monoclinic. The space group is $C^*/C2$ ($C2$, Cm , $C2/m$) and the cell dimensions are $a=15.5878\pm0.0018$ Å, $b=3.7979\pm0.0003$ Å, $c=9.1131\pm0.0013$ Å, $\beta=99.75\pm0.015^\circ$. This unit cell contains 2 ($K_2O \cdot 6TiO_2$).

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論文・Paper

Vaporization of Zinc Oxide from Spinel Solid Solutions

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It was newly found that a larger amount of ZnO vaporizes from $(Zn_{0.5}Co_{0.5})O \cdot 1.3Al_2O_3$ than from $(Zn_{0.5}Ni_{0.5})O \cdot 1.3Al_2O_3$ when heated above $1300^\circ C$.

Cation vacancies tend to occupy B-sites in $(Zn_{0.5}Co_{0.5})O \cdot 1.3Al_2O_3$ and A-sites in $(Zn_{0.5}Ni_{0.5})O \cdot 1.3Al_2O_3$. The difference of vacancy distributions was considered to cause the vapor pressure differences.

Diffusional processes were also considered and it was assumed that Zn^{2+} diffuses outward by way of interstitial sites in $(Zn_{0.5}Co_{0.5})O \cdot 1.3Al_2O_3$, and that the driving force of the

inward diffusion of Co^{2+} or Ni^{2+} is the difference of cation vacancy concentration between the surface and the inside of the pellet. The activation energies of interdiffusion of Zn^{2+} and Co^{2+} , or Zn^{2+} and Ni^{2+} were 110 kcal/mol and 78 kcal/mol, respectively.

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スピネル固溶体からの酸化亜鉛の蒸発

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$\text{ZnO-CoO-Al}_2\text{O}_3$ 系及び $\text{ZnO-NiO-Al}_2\text{O}_3$ 系スピネル固溶体からの ZnO の蒸発現象を調べた。1300°C 以上の高温で加熱した場合、 $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$ の方が、 $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$ よりも ZnO の蒸発が激しい。ペレットからの蒸発量測定によると、ペレット中での Zn^{2+} と Co^{2+} , Zn^{2+} と Ni^{2+} の拡散の活性化エネルギーはそれぞれ 110 kcal/mol, 78 kcal/mol であった。また、スピネル相の加熱処理後の格子定数変化の測定より、拡散過程の考察を行った。X線結晶構造解析を行い、カチオン空位の分布の相違を確認し、この構造の差異と蒸発の関係を推論した。

(10/13/1976 受付)

1. Introduction

There have been several reports on the vaporization phenomena of the spinel solid solution^{1)~3)}. Rutman et al.¹⁾ reported that a stoichiometric $\text{Mg-Al}_2\text{O}_4$ decomposed into MgO (g) and Al_2O_3 (s) at temperatures above 1500°C in vacuum. Lukin et al.²⁾ measured the vaporization rates from stoichiometric sintered spinel bodies in the temperature range 1700~2000°C. Sata et al.³⁾ measured the vaporization rates of MgO from the nonstoichiometric spinel single crystals at temperatures of 1700~1950°C in vacuum and investigated the phase changes in them.

The authors have chosen two kinds of spinel solid solutions in the system $\text{ZnO-Al}_2\text{O}_3$ where ZnO is more volatile than Al_2O_3 ⁴⁾. For one kind 50% of Zn^{2+} sites are substituted by Co^{2+} and for the other by Ni^{2+} , respectively. It was found that a larger amount of ZnO vaporized from the Co-substituted spinel than from the Ni-substituted spinel, when heated at high temperatures above 1300°C.

In general, it is said that both ZnAl_2O_4 and CoAl_2O_4 are normal spinels, but that NiAl_2O_4 is a random one. Therefore, the distributions of cations and cation vacancies in the spinel lattices may naturally be different between Co- and Ni-substituted spinels. And the above phenomenon has been studied from the point of view that the main cause of it may be the difference between the two structures.

In this paper, the vaporization phenomena of the two kinds of spinels, $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$, were made clear, and also the relation between the defect structure and the

vaporization was discussed.

2. Experiment

2.1 Weight loss measurement and EPMA

2.1.1 Samples Zinc oxide, cobalt carbonate, nickel carbonate, aluminum hydroxide of a special grade (Kishida Chemical Co.) were used as starting materials. They were crushed and mixed in an alumina agate mortar, then calcined at 900°C for 24 h in an electric furnace. After the mixing and calcining process was repeated a few times, the spinel powder samples of $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3 \text{Al}_2\text{O}_3$ were prepared. X-ray diffraction measurements were made on these samples and it was ascertained that the homogeneity was achieved in the spinel solid solutions though with poor crystallinity at this stage.

2.1.2 Weight loss measurements These powders were hot-pressed under 240 kg/cm², at 1000°C for 1 h in a carbon mold to make pellets of 10mm in diameter and 2~4mm in thickness. These pellets were calcined at 1200°C for 15 min in air, and weighed by a chemical balance. Diameters and thicknesses of these pellets were measured by a micrometer and the sintering degrees, (apparent density)/(theoretical density), calculated by using a cation vacancy model, were all 45~50%. These pellets were heated at 1300, 1400, 1500°C for 24, 48, 72 h in air and then the weight losses were measured.

2.1.3 EPMA The pellets, heated at 1500°C for 72 h, were buried in resin and their faces, cut by a diamond cutter and polished with SiC abrasives and diamond paste, were used for EPMA measurements.

2.2 X-ray crystal structure analysis

2.2.1 Samples Two more kinds of defect spinels, $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 2\text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 2\text{Al}_2\text{O}_3$, in which vacancy concentration is higher than in $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$ or $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$, were also prepared in the same way as explained in the procedure 2.1.1 to examine cation and cation vacancy distributions in the defective spinel. These powders were sealed in Pt 10% Rh tube, heated at 1750°C for 1 h and then quenched into water. Temperature was measured by an optical pyrometer.

2.2.2 X-ray diffraction On X-ray diffraction measurements $\text{CuK}\alpha$ radiation was used to measure peak intensities. Lattice constants were calculated using reflections from (844) of the spinels with (333) ($d=0.81043\text{ \AA}$, $2\theta=143^\circ 45'$ at 15°C) of MgO as a standard. The data profiles were traced on tracing papers and each piece of paper corresponding to relevant peak was weighed for estimation of its relative peak intensity.

2.2.3 The least square calculation Based on the above data, the crystal structures of $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 2\text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 2\text{Al}_2\text{O}_3$ were analyzed by the least square program which had been modified for X-ray powder diffraction by Yamaguchi et al.^{5)~6)}.

2.3 Measurement of lattice constant

2.3.1. Sample Two types of samples, powdery and pellet, were prepared. In the same method as 2.2.1, the powder samples of $\text{ZnO}\cdot n\text{Al}_2\text{O}_3$, $\text{CoO}\cdot n\text{Al}_2\text{O}_3$, $\text{NiO}\cdot n\text{Al}_2\text{O}_3$, $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot n\text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot n\text{Al}_2\text{O}_3$ ($n=1.0, 1.3, 1.7, 2.0$) were prepared. The powders were pressed to pellet and heated at 1500°C for 72 h for pellet type samples.

2.3.2 X-ray diffraction Lattice constants of the powder samples were measured in the same way as 2.2.2. The pellets were polished from the surface with an SiC abrasive and each face was measured by the X-ray diffractometer.

3. Results and discussions

3.1 Weight loss measurement and EPMA

The dependences of losses in weight of Co- and Ni-substituted spinels on heating time and temperature are shown in Fig. 1. The difference of weight losses between the two spinels is not very large at 1300°C and 1400°C, but it becomes remarkable at 1500°C. The results of EPMA measurements are shown in Fig. 2. The concentration gradient of Zn and Co or Ni is in reverse in both Co- and Ni-substituted spinels. It is clear from this result that Zn vaporizes and $\alpha\text{-Al}_2\text{O}_3$ exsolves on the pellet surfaces, while Co^{2+} or Ni^{2+} diffuses to the inner sites to maintain the spinel structure.

Though the time dependence of weight losses for

Fig. 1. The dependence of losses in weight of $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$ and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$ on heating time at various temperatures.
 $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$: ○; 1300°C, ◐; 1400°C, ◑; 1500°C
 $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$: □; 1300°C, ◑; 1400°C, ■; 1500°C

Fig. 2. Atomic distributions in the pellets of (a) $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$ and (b) $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O}\cdot 1.3\text{Al}_2\text{O}_3$ as a function of the distance from the surface, after heated at 1500°C for 1 h.

the first 24 h is not known, the curves seem to be parabolic after 24 h. This is made more clearly

Fig. 3. Parabolic plots for $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ (—○—) and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ (—●—).

shown in Fig. 3, where the square of the amount of zinc oxide vaporized is plotted against heating time. The vaporization of zinc oxide from the spinel solid solutions is governed by the parabolic law,

$$(\text{weight loss})^2 = kt$$

where k is a rate constant and t , time(hours). In general, this sort of rate constant is expressed by the Arrhenius equation,

$$k = k_0 \exp(-E/RT)$$

where k_0 is a constant; E , the activation energy; R , the gas constant; and T , the absolute temperature. In Fig. 4, $\log k$ is plotted against $1/T$ and nearly straight lines are drawn through the experimental points. The values of E calculated from the slopes of these lines are thought to be an activation energy of the diffusion and the value is 110 kcal/mol for Co-substituted spinel and 78 kcal/mol for Ni-substituted spinel, respectively. These values are thought to be activation energies of the interdiffusion of Zn^{2+} and Co^{2+} , or Zn^{2+} and Ni^{2+} , because the value of the diffusion of Zn^{2+} through the $\alpha\text{-Al}_2\text{O}_3$ out to the surface of the pellet is reasonably thought to be the same for both cases. The diffusion of Zn^{2+} or Ni^{2+} in some kinds of spinel solid solutions has been investigated^{7,9-10}, and the values of activation energy for respective spinels are listed in Table 1. Though the diffusion experiment in the system investigated in the present

Fig. 4. Arrhenius plot of the rate constants for $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ (—○—) and $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ (—●—).

study has not been made, activation energies obtained here are thought to be credible in comparison with those in Table 1.

Table 1. Activation energies for cation diffusion in some spinels.

Spinel	Diffusion species	Activation energy (kcal/mol)
ZnAl_2O_4 ⁹⁾	Zn^{2+}	78
ZnCr_2O_4 ⁹⁾	Zn^{2+}	85.5
ZnFe_2O_4 ⁹⁾	Zn^{2+}	86
NiCr_2O_4 ⁹⁾	Ni^{2+}	74.6
$*(\text{Mg}_{0.9}\text{Ni}_{0.1})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$	Mg^{2+} and Ni^{2+}	63
$-\text{MgO} \cdot 1.3\text{Al}_2\text{O}_3$ ¹⁰⁾		

* The value of activation energy for interdiffusion of Mg^{2+} and Ni^{2+} in the solid reaction is shown.

3.2 X-ray crystal structure analysis and thermodynamical considerations

The results for $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 2\text{Al}_2\text{O}_3$ are shown in Fig. 5. When all the least square parameters were taken in, the calculation did not converge, for the possible reasons that the number of diffraction peaks obtained by $\text{CuK}\alpha$ radiation was too small, and that the difference of atomic scattering factors between Zn and Co was not large enough. Thus, the atomic ratios on each site were fixed, and three parameters of atomic coordinates for oxygen (u -parameter), the overall temperature factor and the scale factor were taken in the least square calculation. R factors were obtained after 3 cycles of calculation. The smaller the R factor is, the nearer the calculated structure to the observed structure, and it has high credibility when R is smaller

Fig. 5. The results of the crystal structure analysis of $(\text{Zn}_{0.3}\text{Co}_{0.3})\text{O} \cdot 2\text{Al}_2\text{O}_3$.

A-site full with cations	cation vacancies distributed	B-site full with cations
●; Co(A)=0.4, ▲; Co(A)=0.4, ■; Co(A)=0.4		
○; Co(A)=0.3, △; Co(A)=0.3, □; Co(A)=0.3		
○; Co(A)=0.1, △; Co(A)=0.1, □; Co(A)=0.1		

than 0.1¹¹⁾. R factor comes to the minimum value down in the right side of Fig. 5, so that both Zn^{2+} and Co^{2+} have a tendency to occupy A-sites and cation vacancies occupy B-sites in the Co-substituted spinel lattice.

The results for $(\text{Zn}_{0.3}\text{Ni}_{0.3})\text{O} \cdot 2\text{Al}_2\text{O}_3$ are shown in Fig. 6. The least square calculation did not converge well for the same reasons as above. Romeijn¹²⁾ reported that the distribution of Ni^{2+} in the system $\text{ZnAl}_2\text{O}_4\text{--NiAl}_2\text{O}_4$ is nearly the same as in the pure NiAl_2O_4 . Datta and Roy¹³⁾, Cooley and Reed¹⁴⁾ observed the cation distribution in NiAl_2O_4 as a function of temperature and found that approximately 50% of Ni^{2+} occupy A-sites and 50% B-sites at our experimental temperature

Fig. 6. The results of the structure analysis of $(\text{Zn}_{0.3}\text{Ni}_{0.3})\text{O} \cdot 2\text{Al}_2\text{O}_3$.

1750°C. And then, the appropriate distribution of Zn^{2+} and Ni^{2+} were fixed as shown in Fig. 6, and the calculation was made changing the amount of Al^{3+} on A-sites. R factors were obtained after 3 cycles of the calculation. B-sites are occupied by cations, and cation vacancies tend to occupy A-sites in Ni-substituted spinel lattice as shown in Fig. 6.

The results are summarized in Table 2. Accord-

Table 2. Cation and cation vacancy distributions of the spinel solid solutions in the systems, $\text{ZnO--CoO--Al}_2\text{O}_3$ and $\text{ZnO--NiO--Al}_2\text{O}_3$.

	Co-substituted spinel	Ni-substituted spinel
A-site	Zn^{2+}	Zn^{2+}
	Co^{2+}	Ni^{2+}
	Al^{3+}	Al^{3+}
		vacancy
B-site	Al^{3+} vacancy	Ni^{2+} Al^{3+}

ing to the theory of Yamaguchi et al.¹⁵⁾, the following equation holds for a particle in the poly-particle system,

$$\tau = 1/p \exp(h/RT)$$

where τ is an activity coefficient; p , vacancy rate; h , partial molar enthalpy; R , the gas constant; T , the absolute temperature. As all the sites in the lattice were considered equal in the process of obtaining the above equation, it is in question to apply it to the spinel solid solution. But if it can be applied independently to A- and B-sites respectively, the difference of vaporization phenomenon between Co- and Ni-substituted spinels would be explained very well as follows.

As to the Co-substituted spinel, A-sites are filled up with cations and the activity of Zn^{2+} is large since there is little cation vacancy around Zn^{2+} , and so the vaporization of ZnO is remarkable. In the Ni-substituted spinel, as there are some cation vacancies around Zn^{2+} , the activity of Zn^{2+} is not very large and the vaporization is mild.

Considering the difference of cation and cation vacancy distributions, it may be proper to assume that Zn^{2+} diffuses outward by way of interstitial sites in Co-substituted spinel, while of vacant sites in Ni-substituted spinel. Therefore, the difference of activation energies obtained in 3.1 seems to be caused by that of diffusional processes.

3.3 Consideration on the diffusional processes from lattice constant measurements

The surface of the pellet of Co-substituted spinel after heated at 1500°C for 72 h was not covered completely with $\alpha\text{-Al}_2\text{O}_3$, and the colors of the surface consisted of blue and white. It is not possible to distinguish with eyes the difference of colors between the surface and the inner part of the pellet

of Ni-substituted spinel. It was all light blue.

Lattice constant changes in the spinel phases of the pellets are shown in **Fig. 7**. Lattice constant decreases from the surface to the interior in the Co-substituted spinel pellet, while it increases in the Ni-substituted spinel pellet. As is clear from

Fig. 7. Lattice constant changes of spinel phases in the pellets as a function of the distance from the surface, (○) for $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ and (●) for $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$.

Fig. 2, the diffusion of Zn^{2+} and Co^{2+} or Ni^{2+} gives rise to the concentration gradient of cations in the pellets, so that the values of lattice constant in Fig. 7 correspond to each spinel phase with a different composition.

In **Fig. 8**, lattice constant changes of spinel solid solutions in the Al_2O_3 -rich side are revealed. It is seen that the lattice constant increases with the increase of the amount ratio $(\text{CoO})/(\text{ZnO})$ in the system $\text{ZnO-CoO-Al}_2\text{O}_3$, while it decreases with the increase of the amount ratio $(\text{NiO})/(\text{ZnO})$ in the system $\text{ZnO-NiO-Al}_2\text{O}_3$, when the mole ratio of Al_2O_3 is fixed constant. Thus, the lattice constant change corresponding to the concentration gradient of cations was observed in the neighborhood of the surface of the pellet.

However, the lattice constant of more than $8.08\text{\AA}$ in the range of about 0.8 mm near the surface of the Co-substituted spinel pellet seems to be a little too large, for the lattice constant should be $8.061 \sim 8.077\text{\AA}$ as is estimated from Fig. 8 if the cation vacancy concentration of the spinel phase was homogeneously constant throughout the pellet. This fact indicates that the cation vacancy concentration near the surface is smaller than in the inside of the pellet, as $\alpha\text{-Al}_2\text{O}_3$ exsolves on the surface with the vaporization of ZnO . Therefore,

Fig. 8. Lattice constants of the spinel solid solutions in the Al_2O_3 rich side.
○; $\text{CoO-Al}_2\text{O}_3$, ●; $\text{ZnO-Al}_2\text{O}_3$, ●; $\text{NiO-Al}_2\text{O}_3$,
---; $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O-Al}_2\text{O}_3$, ---; $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O-Al}_2\text{O}_3$

it can be assumed that the difference of the cation vacancy concentration between near the surface and in the inner part is a driving force of the inward diffusion of Co^{2+} . For Ni-substituted spinel, the vacancy concentration difference cannot be derived from Fig. 8, as the lattice constant changes only from 8.044 to $8.047\text{\AA}$ near the surface of the pellet. But, it would be logical to consider there is a vacancy concentration difference in the pellet, because a small amount of exsolved $\alpha\text{-Al}_2\text{O}_3$ was detected on the surface by the X-ray diffractometer, and it should be a driving force of the inward diffusion of Ni^{2+} .

4. Summary

A larger amount of ZnO vaporized from $(\text{Zn}_{0.5}\text{Co}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$ than from $(\text{Zn}_{0.5}\text{Ni}_{0.5})\text{O} \cdot 1.3\text{Al}_2\text{O}_3$, when heated at high temperatures above 1300°C .

The possible reason for this phenomenon is that the activity of Zn^{2+} on A-site is different between the two spinels since cation vacancies tend to occupy B-sites in Co-substituted spinel and A-sites in Ni-substituted spinel.

It was assumed that Zn^{2+} diffuses outward by way of interstitial sites in Co-substituted spinel, while of vacant sites in Ni-substituted spinel, and the activation energies were calculated to be 110 kcal/mol and 78 kcal/mol , respectively.

The results support the suggestions that the cation vacancy concentration difference between near the surface and in the inside of the pellet is

a driving force of the inward diffusion of Co^{2+} or Ni^{2+} .

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訂 正

窯業協会誌 85 [2] 96-99 (1977)「磷酸カルシウム-弗化物系の加熱反応 (英文)」金澤孝文他, の本文を下記のよう
に訂正し, ここにお詫び致します.

項 目	誤	正
85 [2] 1977		
本文 5 ページ右下 13 行目 同上	phospahte	phosphate
本文 96 ページ最下行 同上	受理日脱落	(6/9/1976 受付)
本文 98 ページ左 3 行目	Fig. 2. seen	Fig. 2 is also seen