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Synthesis and Thermal Stability of Polycrystalline New Divalent β''- and β-Ferrites Prepared by Ion Exchange

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Using ion-exchange chemistry the divalent cations Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Sn^{2+} have been substituted for K^+ in polycrystalline CdO-stabilized K-β''-ferrite samples. Ba, Sr, Ca, Mg, Pb, and Cd ion exchange led to the synthesis of new materials, the divalent M^{2+}-β''-ferrites (M = Ba, Sr, Ca, Mg) and M^{2+}-β-ferrites (M = Cd, Pb), respectively. Co^{2+}-diffusion resulted in the formation of a spinel-type Co-ferrite. In the case of Zn, Mn, Fe, and Sn the samples decomposed to α-Fe_2O_3. The thermal stability of the new divalent β''- and β-ferrites was studied either by high-temperature exchange reactions or by air annealing of the exchanged products. Ba- and Sr-β''-ferrites and Pb-β-ferrite converted to M-type hexagonal ferrites with the magnetoplumbite structure. Mg-β''-ferrite decomposed to a spinel-type Mg-ferrite, and Ca-β''-ferrite and Cd-β-ferrite decomposed to α-Fe_2O_3. Composition, lattice parameters, SEM photographs, and magnetic properties of the ferrites formed are given. The magnetic susceptibilities of the divalent β''- or β-ferrites have values between 0.63 and 1.14×10^{-4} emu/g · Oe at room temperature.

1. Introduction

It is well known that the entire sodium ion content of the solid electrolyte β''-alumina can be replaced by a variety of mono-, di-, and trivalent cations (*1, 2*). β''-Alumina has a unit cell which crystallizes into the trigonal system. Due to its unusual structure consisting of three alkali layers and an ≈11-Å-thick slab of close-packed oxygen layers, in which aluminum ions occupy octahedral and tetrahedral interstitial sites, the so-called "spinel blocks," β''-alumina presents exceptional ion-transport properties. In particular, complete or partial rapid ion exchange occurs for at least 12 divalent cations (Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Pb^{2+}, Mn^{2+}, Eu^{2+}, Ni^{2+}, Co^{2+}, Sn^{2+}, and Hg^{2+}) (*2*), leading to the synthesis of various divalent β''-aluminas. The divalent β''-aluminas have been extensively studied for their ionic conductivity and other properties (*3–13*).

In the K_2O–Fe_2O_3 system there is an analog of β''-alumina, the β''-alumina-type, K^+-β''-ferrite. Because of its instability, i.e., the difficulty of preparation (*14*), the properties of β''-ferrite have been studied only in the last few years (*14–19*). For preparation of the Na^+-β''-alumina, usually $Na_{1.67}Al_{10.33}M^{2+}_{0.67}O_{17}$, it is well known that the β'' phase decomposes at >1500°C (*20*), but it is stabilized by doping with a divalent cation (Mg^{2+}, Ni^{2+}, Zn^{2+}, etc.) (*21*). Pure single crystals of K-β''-ferrite stabilized by CdO

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were obtained using K_2O–KF–B_2O_3 as a flux (*22*) and those of mixed (Na, K)-β''-ferrite stabilized by ZnO, CoO, or NiO were obtained from a $NaFeO_2$ flux (*16–18*). However, polycrystalline β''-ferrite is generally formed with the β phase depending on the kind and amount of stabilizing agent (*14*). The unit cell of the more stable β phase, $K_{1+x}Fe_{11}O_{17}$, $x = 0$ to 1 (*23*), consists of two spinel blocks and two alkali layers that crystallize into the hexagonal system.

K^+-β''-ferrite is known to be a mixed ionic and electronic conductor (*14*). An attempt to extend ion-exchange chemistry in the β''-alumina-like β''-ferrites started a few years ago. It was found that monovalent ions such as Na^+, K^+, Rb^+, Cs^+, Tl^+, NH_4^+, H^+, and H_3O^+ diffuse rapidly to form various M^+-β''-ferrites (*15, 24–27*). On the contrary, ionic exchange reactions with the divalent Ba^{2+} or Sr^{2+} led to a phase transformation to nonstoichiometric *M*-type ferrites (*25–27, 28*). In this work a detailed study using an ionic exchange procedure with 11 divalent cations (Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Sn^{2+}) on K^+-β''-ferrite is presented. Since the previous experiments with Ba and Sr were performed at high temperatures, 700–800°C, low exchange reaction temperatures were used, between 200 and 500°C, to prevent phase transitions, i.e., to obtain the corresponding M^{2+}-β''-ferrites. In fact, Ba, Sr, Ca, Mg and Pb, Cd ionic exchange resulted in the synthesis of new materials, the divalent β''- and β-ferrites respectively. As far as we know, this is the first report on the synthesis of such materials. The study of the thermal stability of the divalent ion-exchange derivatives by means of ionic exchange reactions at high temperatures, 500–800°C, or by annealing of the resulting divalent β'' or β phases, is presented. It is shown that M^{2+}-β''- or β-ferrites are metastable compounds, which either convert to the thermodynamically more stable *M*-type or spinel-type ferrites or decompose to α-Fe_2O_3 at various temperatures. The exchange reactions with monovalent ions or with Ba^{2+}, Sr^{2+} at high temperatures, reported in the earlier studies, were performed on β''-ferrite single crystals. In this work all ionic exchange reactions were performed on single-phase polycrystalline β''-ferrites, i.e., K^+-β''-ferrite stabilized by Cd^{2+}. Since ionic exchange with several divalent ions on K^+-β-ferrite has resulted also in phase transition phenomena (*23*), the low-temperature ionic exchange procedure could provide an understanding of the conditions appropriate to the preparation of divalent derivatives of K^+-β-ferrite as well.

The magnetic behavior of β''-ferrite is somewhat unusual. The study of the thermal variation of the reciprocal susceptibility (*16*) shows that, since a Néel hyperbola, characteristic of an antiferromagnet with more than two equivalent sublattices, is observed at high temperatures, 800–1000 K, the lower-temperature part of the curve shows no minimum as a typical $\chi_{\parallel}^{-1}(T)$, nor stabilization as in the case for $\chi_{\perp}^{-1}(T)$, indicating a magnetic order point. The same behavior has been reported for $\chi_{\perp}^{-1}(T)$ in K^+-β-ferrite (*29*) and has been explained as resulting from a planar antiferromagnetic arrangement consisting of ferrimagnetic spinel blocks negatively coupled between them (Gorters' "antiferrimagnetism"). On the other hand, neutron diffraction study provided evidence of the existence of two superimposed magnetic modes, an antiferromagnetic and a weak ferromagnetic (*18*). The presence of the latter has been explained as due to the incorporation of hydronium cations in the conduction planes which modifies the exchange integrals of the Fe^{3+} cations in the Fe(3) sublattice, thus affecting the complete antiferromagnetic coupling between the neighboring ferrimagnetic sublattices. In this work some magnetic measurements on the exchange derivatives are reported, not by means of the magnetic characterization of the materials but as an indirect method to control the retainment of the β''-type structural arrangement or to understand some aspects of the process of the phase transitions observed.

2. Experimental Procedure

Polycrystalline K^+-β''-ferrite is usually formed together with the β phase, the fraction $f(\beta'')$ of β'' phase produced depending on the kind and amount of stabilizing agent (*14*). Therefore a series of samples were prepared to obtain single phases of β''-ferrite to be used as starting material. K_2CO_3, Fe_2O_3, and MO were mixed in a molar ratio $1:(6-x):x$, $M = Cd^{2+}, Ca^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}$ and $x = 0.25/0.50/0.75/1.0$. Since the β and β'' phases can exist in a large composition range (*30*), the proportion proposed in Ref. (*30*) was chosen. Alkali vaporization is unavoidable during the heating process. Therefore, an excess of K_2CO_3 was used in the starting mixture. After homogenization in a ball mill using ethanol as a dispersing agent and drying at 150°C for 24 hr, every mixture was heated at 950°C for 1 hr in a porcelain crucible.

X-Ray powder diffraction was used to check whether the products were single-phase β''-ferrite. The relative amount of β'' phase was estimated by the formula

$$f(\beta'') = \frac{I_{\beta''}(1\,0\,11)}{I_{\beta''}(1\,0\,11) + I_{\beta}(1\,0\,7)} \qquad (1)$$

where I is the intensity of the characteristic peaks of the β'' and β phases, respectively (*31*). To more accurately calculate the integrated intensities these peaks were measured with a slow scanning rate, 1°/8 min.

The composition of the products was determined by electron microprobe (EDAX). The magnetic measurements were made by means of a vibrating sample magnetometer and a Faraday balance at room temperature.

The M^{2+} ions investigated for ion exchange were Ba^{2+}, Sr^{2+}, Ca^{2+}, Mg^{2+}, Cd^{2+}, Pb^{2+}, Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Sn^{2+}. The exchanges were carried out in a platinum crucible and were contained within a box furnace having an air atmosphere. In some cases the ion-exchange reaction was performed *in vacuo* or in an argon atmosphere to maintain the oxidation state of the ion introduced into the sample. Powder of K^+-β''-ferrite (0.2–1 g) was soaked into the appropriate salts, nitrates or chlorides or their eutectic mixtures (5–10 g), for various durations between 15 min and 4 hr. The salts or eutectic mixtures were chosen (*32*), in the first place, so that they melt at temperatures as low as possible, 200–500°C, to avoid structure transformation during ion exchange. In some cases the exchange treatment was carried out at higher temperatures, 500–800°C, to study the stability of the phases formed. For the same purpose a series of samples were annealed at 1000°C for 24 hr in an air atmosphere. After the exchange treatment the samples were allowed to air cool and the salt coating was dissolved in deionized water. The exchange products were filtered through a 0.2-μm paper filter using a water jet filter pump. After filtration the samples were rinsed in acetone and allowed to dry at 120°C for 2 hr. Table I summarizes the exchange procedures.

The exchange products were identified by the X-ray powder diffraction method using Cu$K\alpha$ radiation and Si as an internal standard. The lattice constants were calculated by least-squares refinement. The composition of the products was determined by means of electron microprobe (EDAX). Since this is a semiquantitative method, and was the only one available, the compositions of the exchanged products, given in Table III, are indicative and used to estimate the extent of K^+ substitution. Scanning electron microscopy was used to study the quality of the particles after ion exchange.

For the samples exchanged with Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Cd^{2+}, in which the β'' phase was retained, the magnetic sus-

TABLE I

EXCHANGE PROCEDURES

Ion	Melt composition[a] (mole %)	Temperature (°C)	Time	K^+ replaced (%)	Atmosphere
Ba^{2+}	$Ba(NO_3)_2 : KNO_3$ (20 : 80)	360	2 hr	88	Air
	$Ba(NO_3)_2 : KNO_3$	350	4 hr	95	Air
	$BaCl_2 : KCl$ (40 : 60)	800	30 min	100	Air
	$BaCl_2 : KCl$	800	2 hr	98	Air
Sr^{2+}	$Sr(NO_3)_2 : KNO_3$ (22 : 78)	350	1 hr	92	Air
	$Sr(NO_3)_2 : KNO_3$	350	4 hr	89	Air
	$SrCl_2 : KCl$ (70 : 30)	700	45 min	100	Air
	$SrCl_2 : KCl$	700	2 hr	100	Air
Pb^{2+}	$Pb(NO_3)_2 : KNO_3$ (50 : 50)	280	1 hr	97	Air
	$Pb(NO_3)_2 : KNO_3$	290	2 hr	97	Air
	$PbCl_2 : KCl$ (80 : 20)	500	45 min	84	Air
	$PbCl_2$	650	1 hr	—	Air
Ca^{2+}	$Ca(NO_3)_2 : NaNO_3$ (40 : 60)	310	30 min	90	Air
	$Ca(NO_3)_2 : NaNO_3$	310	2 hr	92	Air
	$Ca(NO_3)_2 : NaNO_3$	330	4 hr	100	Air
	$CaCl_2 : KCl$	700	30 min	100	Air
Cd^{2+}	$Cd(NO_3)_2 : NaNO_3$ (65 : 35)	200	1 hr	96	Air
	$Cd(NO_3)_2 : NaNO_3$	200	2 hr	100	Air
	$CdCl_2$	600	1 hr	100	Air
Mg^{2+}	$Mg(NO_3)_2 : NaNO_3$	200	1 hr	88	Air
	$Mg(NO_3)_2 : NaNO_3$ (50 : 50)	200	4 hr	98	Air
	$MgCl_2 : KCl$ (40 : 60)	480	1 hr	90	Air
Co^{2+}	$CoCl_2 : KCl$ (44 : 56)	400	1 hr	86	Argon
	$CoCl_2 : KCl$	450	1 hr	93	Vacuum
Mn^{2+}	$MnCl_2 : KCl$ (36 : 64)	500	1 hr	100	Vacuum
Zn^{2+}	$ZnCl_2 : KCl$ (54 : 46)	280	45 min	90	Air
Sn^{2+}	$SnCl_2 : KCl$ (63 : 37)	300	15 min	100	Air
Fe^{2+}	$FeCl_2 : NaCl$ (44 : 56)	430	1 hr	—	Argon

[a] From Ref. (*32*).

ceptibility was measured with the Faraday balance at room temperature. When the samples revealed high magnetization caused by a phase transformation, magnetic measurements, by means of a SQUID magnetometer at 3 K applying 50 kOe of magnetic field, were performed.

3. Results and Discussion

3.1. Starting Material

Table II shows the relation between the β''-phase fraction and the *M*O additive. The results for the Cd^{2+}- and Ca^{2+}-stabilized samples are in agreement with Ref. (*14*). The other results present some discrepancy compared with those reported in Ref. (*14*), with respect to the Mg^{2+}-, Zn^{2+}-, and Cu^{2+}-stabilized samples. In the work presented here it was found that $f(\beta'')$ is almost independent of the concentration of ZnO and MgO additive and is between 40 and 60%, with the exception of MgO/0.25 for which $f(\beta'')$ was 10%. In contrast, Nariki *et al.* reported that the additive effect of MgO and ZnO gave decreased values with x, and $f(\beta'')$ was between 10 and 20%. In the case of

Cu^{2+} in Ref. (*14*), $f(\beta'')$ was found to increase with x but the β phase disappeared only when $x = 2.0$ and the by-product Cu Fe_2O_4 was formed when $x > 1.0$. In this work a CuO-stabilized sample with $x = 0.75$ was found to be single β'' phase without any traces of by-products.

Our results are in better agreement with those in Ref. (*33*) where the formation of ≈50% β'' phase is reported for samples stabilized by Cd^{2+}, Ni^{2+}, Zn^{2+}, Mg^{2+}, and Co^{2+}, but no other *M*O concentration is reported apart from $x = 0.25$.

Nevertheless, as shown in Table II at least four samples were found to form single-phase K^+-β''-ferrite. The CdO-stabilized sample with $x = 0.75$ was chosen as a starting material for all ionic exchange reactions in this work. The magnetic susceptibility of this sample was 0.66×10^{-4} emu/g · Oe at room temperature, in very good agreement with other literature values for Co^{2+}-, Ni^{2+}-, and Zn^{2+}-stabilized, mixed (Na, K)-β''-ferrite single crystals (*16, 25*): 0.60, 0.40, and 0.66×10^{-4} emu/g · Oe, respectively.

The chemical composition determined was $K_{1.38}Fe_{10.6}Cd_{0.4}O_{17}$. This formula was deduced considering that the total Fe + Cd atoms p.f.u. must be equal to 11, as conditioned by the number of available crystallographic sites for this structure. Such a formula is close to the composition $K_{1.33}Fe_{10.27}Cd_{0.73}O_{16.87}$, determined by Nariki *et al.* by means of X-ray single-crystal structure analysis (*22*), at least with respect to K^+ content. Regarding the Cd content, this result is not consistent with the stoichiometry of the starting mixture which, however, gives a sum Fe + Cd = 11.25. Nevertheless, the calculation of the chemical formula, according to the stoichiometry of the starting mixture, gives $K_{1.42}Fe_{10.5}Cd_{0.75}O_{16.84}$, i.e., the same K^+ content. Chemical analysis showed that the Cd content was 3–3.5 at.%, both in the parent compound and in all ion-exchange derivatives, for more than 30 different measurements. Since the initial amount of Cd atoms was 6% in the starting mixture, this difference cannot be attributed to the measurement itself. CdO decomposes at 900°C, which is the melting point of the oxide. Since the solid-state reaction was carried out at 950°C, the alternative assumption of a loss of Cd during the firing cannot be excluded. On the basis of these results, the following compositions are described assuming that Fe + Cd = 11.

The calculated lattice parameters were $a = 5.974(2)$ and $c = 35.74(3)$ Å.

TABLE II

EFFECT OF THE MO ADDITIVE, $K_2O:(6 - x)Fe_2O_3:xMO$,[a] ON THE FORMATION OF K^+-β''-FERRITE (950°C)

	Yield $f(\beta'')$ (%)					
x	Cd	Mg	Zn	Ni	Ca	Cu
0.25	40	10	60	65		
0.50	60	50	60	60	100	
0.75	100	40	60	65	100[b]	100
1.00	80[c]	40	55	60	100	

[a] Composition of the starting mixture.

[b] $CaFe_2O_4$ as a by-product.

[c] $CdFe_2O_4$ as a by-product.

3.2. Ionic Exchange

Table III shows the results of the ion exchange of potassium ions in the K^+-β''-ferrite powder with divalent cations. The substitution of the K^+ ions is very fast in all cases and reaches 90–100% completion in very short times. These results indicate that the exchange products must be divided into three groups:

i. Ion exchange of potassium with Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Cd^{2+} at low temperatures, 200–350°C, led to the synthesis of various M^{2+}-ferrites with β''- or β-type structure.

ii. Ion exchange with the same cations but

TABLE III

RESULTS FROM ION EXCHANGE OF K^+-β''-FERRITE WITH VARIOUS DIVALENT IONS

Ion	Temperature (°C)	Time (hr)	Phase (a.e.)[a]	Composition	M_{50}[b] (emu/g)	M_{50}[c] (emu/g)	M_0[d] (emu/g)	Phase (a.a.)
K				$K_{1.4}Fe_{10.6}Cd_{0.4}O_{17}$[e]	a.f.			
Ba1	360	2	β''	$Ba_{0.65}K_{0.17}Fe_{10.6}Cd_{0.4}O_{17}$	a.f.	76.3	98	M + ?
Ba2	350	4	β''	$Ba_{0.64}K_{0.07}Fe_{10.6}Cd_{0.4}O_{17}$	a.f.			
Ba3	800	0.5	M	$Ba_{0.85}Fe_{10.6}Cd_{0.4}O_{17.2}$	58.6	85.4	98	M
Ba4	800	2	M	$Ba_{0.93}K_{0.02}Fe_{10.6}Cd_{0.4}O_{17.2}$	63.4	88.9	98	M
Sr1	350	1	β''	$Sr_{0.48}K_{0.12}Fe_{10.6}Cd_{0.4}O_{16.9}$	a.f.			
Sr2	350	4	β''	$Sr_{0.56}K_{0.12}Fe_{10.6}Cd_{0.4}O_{17}$	a.f.			
Sr3	700	0.75	M	$Sr_{0.87}Fe_{10.6}Cd_{0.4}O_{17.2}$	65.1	90.9	104	M
Sr4	700	2	M	$Sr_{0.87}Fe_{10.6}Cd_{0.4}O_{17.2}$	79.4	91.0	104	M
Pb1	280	1	β	$Pb_{0.9}K_{0.04}Fe_{10.6}Cd_{0.4}O_{17.2}$	a.f.			
Pb2	290	2	β	$Pb_{0.9}K_{0.04}Fe_{10.6}Cd_{0.4}O_{17.2}$	a.f.			
Pb3	500	0.75	β	$Pb_{1.1}K_{0.22}Fe_{10.6}Cd_{0.4}O_{17.5}$	22.4	73.6	88	M + Fe_2O_3
Pb4	650	1	Fe_2O_3					
Ca1	310	0.5	β''	$Ca_{0.48}K_{0.14}Fe_{10.6}Cd_{0.4}O_{16.9}$	a.f.			
Ca2	310	2	β''	$Ca_{0.54}K_{0.11}Fe_{10.6}Cd_{0.4}O_{16.9}$	a.f.			
Ca3	330	4	β''	$Ca_{0.76}Fe_{10.6}Cd_{0.4}O_{17}$	a.f.			
Ca4	700	0.5	Fe_2O_3 + S + β''					
Cd1	200	1	β	$Cd_{0.4}K_{0.05}Fe_{10.6}Cd_{0.4}O_{16.7}$	a.f.			
Cd2	200	2	β	$Cd_{0.44}Fe_{10.6}Cd_{0.4}O_{16.8}$	a.f.			
Cd3	600	1	Fe_2O_3 + S					
Mg1	200	1	β''	$Mg_{0.44}K_{0.17}Fe_{10.6}Cd_{0.4}O_{16.8}$	a.f.			
Mg2	200	4	β''	$Mg_{0.57}K_{0.03}Fe_{10.6}Cd_{0.4}O_{16.9}$	a.f.			
Mg3	480	1	S + β''	$Mg_{0.65}K_{0.01}Fe_{2.3}Cd_{0.04}O_{4+x}$	34.2	49.4	62	S + Fe_2O_3
Co1	400	1	S	$Co_{0.47}K_{0.05}Fe_{2.4}Cd_{0.07}O_{4+x}$	38.4	65.4	94	S + Fe_2O_3
Co2	450	1	S + Fe_2O_3	$Co_{0.43}K_{0.02}Fe_{2.5}Cd_{0.04}O_{4+x}$	42.7	52.5	94	S + Fe_2O_3
Mn1	500	1	Fe_2O_3 + S					
Zn1	280	0.75	Fe_2O_3 + β'' + S					
Sn1	300	0.25	?					
Fe1	430	1	Fe_2O_3					

[a] a.e., after exchange; a.a., after annealing; a.f., antiferromagnetic; M, magnetoplumbite; S, spinel; β'',β''-ferrite; β,β-ferrite; ?, unidentified phase.

[b] Magnetization at 50 kOe/3 K before annealing.

[c] Magnetization at 50 kOe/3 K after annealing.

[d] From literature reference, saturation magnetization at 0 K.

[e] K^+-β''-ferrite starting material as determined by chemical analysis.

at relatively high temperatures, 500–800°C, resulted in either a phase transition or decomposition of the samples. Ba^{2+}-, Sr^{2+}-, and Pb^{2+}-exchanged products were transformed to a modified M-type hexagonal ferrite. In the case of the Mg^{2+} product the β'' structure was rearranged to form a spinel-type ferrite, and the Ca^{2+} and Cd^{2+} samples were decomposed to α-Fe_2O_3.

iii. The products from ion exchange with Co^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, and Sn^{2+} belong to a third group. Although relatively low temperatures were used, 280–500°C, the formation of the corresponding M^{2+}-β''-ferrites was not achieved. The Co^{2+}-exchanged product showed a phase transition to a spinel-type ferrite. Ionic exchange with Zn^{2+}, Mn^{2+}, and Fe^{2+} led to the decomposition of the samples to α-Fe_2O_3 and ionic exchange with Sn^{2+} led to an unidentified phase.

3.2.1. M^{2+}-β''- and β-Ferrites

As shown in Fig. 1, the appearance of the exchanged products that retained the β''-type structure was not affected by the ion exchange treatment. The X-ray diffraction patterns of these products were similar to those of the K^+-β''-ferrite. Table IV shows the lattice constants of the exchanged β''-ferrite samples. It is known that the c_0 value, which indicates the thickness of the alkali

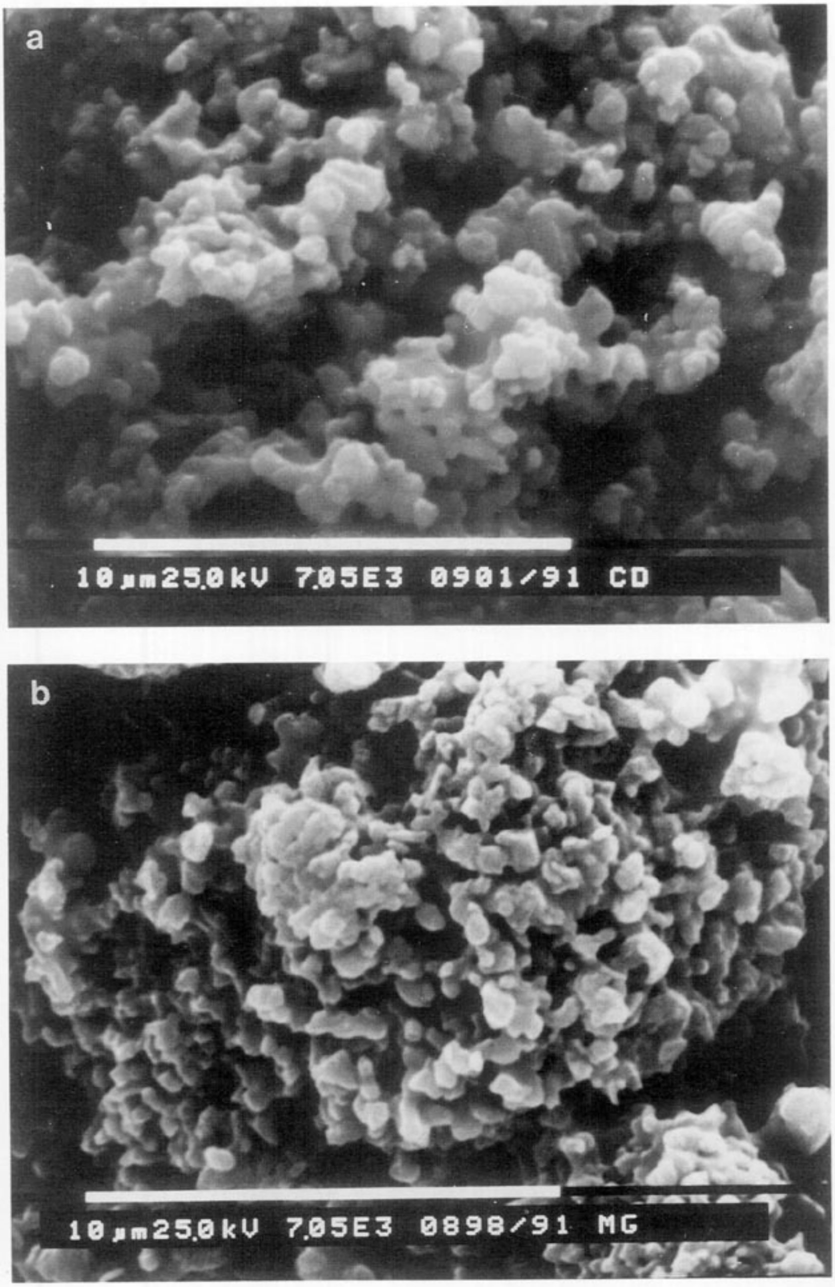

FIG. 1. SEM photographs of K^+-β''-ferrite powder before ion exchange (a) and after ion exchange with Mg^{2+}, sample Mg2 (b).

layer, depends on the ionic radii of the elements in the alkali layers; i.e., the larger the ion the greater the c_0. For the materials discussed in this work, preliminary TG-DTA measurements (*34*) showed weight losses, 1–4%, between 100 and 250°C, indi-

TABLE IV

LATTICE PARAMETERS AND MAGNETIC SUSCEPTIBILITY AT ROOM TEMPERATURE OF THE DIVALENT β''- AND β-FERRITE EXCHANGE PRODUCTS

Product	Ionic radius (Å)	a_0 (Å)	c_0 (Å)	χ (RT) ($\times 10^{-4}$ emu/g · Oe)	Ref.
(Na, K)-β''-ferrite[a]		5.959(1)	35.88(2)	0.60	(*16*)
K^+-β''-ferrite[b]		5.968	35.78		(*14*)
K^+-β''-ferrite	1.33	5.974(2)	35.74(3)	0.66	[c]
Ba^{2+}-β''-ferrite	1.35	5.970(2)	36.00(3)	0.63	[c]
Sr^{2+}-β''-ferrite	1.12	5.979(1)	35.80(2)	1.04	[c]
Ca^{2+}-β''-ferrite	0.99	5.964(1)	35.63(2)	0.98	[c]
Mg^{2+}-β''-ferrite	0.65	6.029(2)	35.93(3)	1.08	[c]
K^+-β-ferrite		5.933(2)	23.81(2)	0.46	(*29*)
Pb^{2+}-β-ferrite	1.20			0.83	[c]
Cd^{2+}-β-ferrite	0.97			1.14	[c]

[a] Co^{2+}-stabilized single crystal.
[b] Cd^{2+}-stabilized single crystal.
[c] This work.

cating the presence of H_3O^+ cations on the conduction plane. The incorporation of hydronium ions into the conduction planes of β- and β''-alumina exposed to moist air has been proven by several authors (*35*). Carbarczyk *et al.* showed that the extent of hydronium incorporation increases with decreasing ionic radius of the ion introduced (*36*). Since the samples were kept in air, it was deduced that the incorporation of H_3O^+ cations with a large ionic radius, 1.40 Å, resulted in increased c_0 values for the exchanged products, in particular for the Mg-exchanged sample which is the smallest. It is characteristic that the weight loss observed for this sample had the largest value, ≈4%. On the other hand, the distribution of the divalent cations on the conducting plane and the locations of the O(5) column oxygens may influence the *c*-lattice spacing of the crystals. Alden *et al.* predicted that the Ba atoms occupy only the 6*c*-(BR) sites in Ba^{2+}-β''-alumina, whereas Ca atoms occupy both the 6*c*- and the 9*d*-(*m*O) sites in Ca^{2+}-β''-alumina (*37*).

In the case of Pb^{2+}- and Cd^{2+}-exchanged products only low and rather broad peaks were observed, indicating that the samples were largely amorphous. The peak at $d \approx 2.75$ Å (1 0 11) characteristic of the β'' phase almost disappeared and a new peak at $d \approx 2.83$ Å was observed for the last two samples. As this peak is characteristic of the β phase (1 0 7) it was assumed that ion exchange with Pb^{2+} and Cd^{2+} led to the formation of the corresponding M^{2+}-β-phase.

Chemical analysis showed that substitution of the potassium ions by the divalent Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Cd^{2+} cations was ≈2 : 1 in accordance with the electrostatic neutrality condition. The number of Fe and Cd atoms p.f.u. as well as the ratio Fe/Cd, before and after ion-exchange reaction, remained constant.

Magnetic measurements strengthened the assumption that substitution of K^+ ions by the above-mentioned divalent cations leads to synthesis of the corresponding M^{2+}-β''- or M^{2+}-β-type ferrites. In fact, M(H) curves recorded by means of a VSM at room temperature showed that the exchanged products presented similar magnetic behavior to the starting K^+-β''-ferrite. Magnetic susceptibilities measured with the Faraday balance at room temperature are given in Table IV. These values are on the order of 10^{-4} emu/g · Oe, the value of the starting material. The fact that they are slightly higher may be due to the presence of a superimposed weak ferromagnetic component which was observed from the M(H) curves, except for the Ba^{2+}-exchanged samples. The saturation magnetization values were between 0.3 and 0.6 emu/g. Such a weak ferromagnetic component has been observed in the cases of NH_4^+-, Ag^+- and Cs^+-ferrite (*23*) and Na^+-β''-ferrite (*16, 18*). It has been shown that Na^+-β''-ferrite acquires a weak spontaneous magnetization due to the incorporation of hydronium cations into the conduction plane (*18*). As already mentioned, TG-DTA measurements indicated the presence of such cations in the materials studied here. Thus, the increase in the susceptibility could be attributed to a hydration effect.

3.2.2. Thermal Stability of the M^{2+}-β''- and M^{2+}-β- Products

a. Ba, Sr, and Pb. The ionic exchange treatment with Ba^{2+}, Sr^{2+}, Pb^{2+}, Mg^{2+}, Ca^{2+}, and Cd^{2+} ions at higher temperatures, 500–800°C, resulted in the transition of the initial rhombohedral β'' structure of the starting material. The Ba-, Sr- and Pb-exchanged products converted to a modified M-type hexagonal ferrite. Ionic exchange reactions with Ba^{2+} and Sr^{2+} on Co-stabilized single crystals of (Na, K)-β''-ferrite (*28*) and with Sr^{2+} and Pb^{2+} on Cd-stabilized single crystals of K-β-ferrite (*23*), at temperatures between 600 and 1000°C, have been reported to result in the formation of M-type ferrites. However, the presence of the stabilizing divalent cation, substituting a Fe^{3+} cation, excludes the chemical formula $BaFe_{12}O_{19}$ of M-ferrite. The synthesis of a Co^{2+}-substituted Ba-M ferrite has been reported but only by means of the simultaneous substitution of two Fe^{3+} cations by a Co^{2+}, Ti^{4+} pair (*38*). Based on X-ray crystal structure analysis data a model which describes the unit cell as an intergrowth of M-type and β-alumina-type unit cells in the proportion 3 : 1 has been proposed for a high-temperature Ba-exchanged Co-stabilized (Na, K)-β''-ferrite single crystal (*40*).

In fact, for the Ba and Sr products the phase transition was completed during ion exchange as found from the X-ray diffraction patterns where only peaks corresponding to the M phase were observed. Substitution of the K^+ ions by Ba^{2+} or Sr^{2+} was 100%, contrary to the low-temperature exchanged Ba or Sr products, where the K^+ substitution reached values between 88 and 95%. Another difference was that the inserted Ba^{2+} or Sr^{2+} ions exceeded the ratio $K^+ : M^{2+} = 2 : 1$ expected from the electrostatic neutrality condition. As the number of Fe and Cd atoms and the ratio Fe/Cd remained constant, before and after exchange, this ratio was calculated to be $\approx 2 : 1.4$.

No effect of the duration of the exchange reaction was observed on the X-ray diffraction patterns or on the amount of inserted ions, apart from a slight increase in the amount of inserted Ba with reaction duration. On the contrary the magnetization values were found to increase with the duration of the exchange reaction.

Magnetic measurements by means of M(H) curves at 3 K at an applied field of 50 kOe confirmed the phase transformation. The products revealed high magnetization values but saturation was not reached even at 50 kOe. As shown in Table III the M_{50} values increased with the duration of the exchange reaction. That increase must not be attributed to an increase in the amount of inserted Ba or Sr itself. This fact was more clear in the case of Sr-exchanged material. In the sample Sr3 exchanged for 45 min and the sample Sr4 exchanged for 2 hr the same content of Sr was found by chemical analysis, i.e., 0.87 Sr atom p.f.u., but M_{50} values were 65.1 and 79.4 emu/g, respectively. In the case of Ba, sample Ba3 exchanged for 30 min contained almost the equivalent M^{2+} amount as the Sr samples, 0.85 Ba atom p.f.u., and M_{50} was 58.6 emu/g. Sample Ba4 contained 0.93 Ba atom p.f.u. but the increase in M_{50} to 63.4 emu/g is not proportional to that of the equivalent Sr-exchanged material. It was assumed that the increase in M_{50} with exchange reaction time must be attributed to the decrease in defects present in short-time exchange products due to an annealing effect caused by long-time exchange reactions. The presence of such defects was also indicated from the X-ray patterns of the short-time products, where only low and rather broad peaks were observed, showing that the products were largely amorphous.

This assumption was strengthened from the annealing of each sample at 1000°C for 24 hr in air. First, the diffraction peaks of the annealed samples became higher and sharper. The samples were much closer to saturation as M_{30} differed only 1.5–2% from M_{50}, this difference being 5–7% for the samples before annealing. It is remarkable that the samples Ba3, Sr3, and Sr4 having 0.87 Ba(Sr) atom p.f.u. reached such M_{50} values, which correspond to 87.5% of the saturation values at 0 K of the pure Ba- and Sr-M-ferrites, respectively. Sample Ba4, with 0.93 Ba atom p.f.u., reached an M_{50} value 91% that of Ba–M-ferrite. Though the difference in Ba content between samples Ba3 and Ba4, as determined by chemical analysis, was 9%, which is at the limits of experimental error in electron microprobe, it was logical to assume that the increased M_{50} value of the annealed Ba4 sample indicates that the latter is richer in M phase than the annealed Ba3 sample. On the other hand, Sr3 and Sr4, containing the same amount of Sr atoms, reached the same value of M_{50} after annealing.

To understand whether the phenomenon of phase transition was due to the ion-exchange procedure a Ba-β''-product (short-time exchanged sample Ba1) was annealed at 1000°C for 24 hr. This annealed sample was also converted to an M-type ferrite as determined by the X-ray diffraction pattern and the magnetic measurements. The β'' phase disappeared and the magnetic behavior of the sample was dramatically altered. The Ba-β''-type sample revealed a high spontaneous magnetization and reached a value of 76.3 emu/g at 50 kOe. The latter is considerably lower than that of the high-temperature exchange products after annealing. However, sample Ba1 of the β'' type contained fewer Ba atoms p.f.u., 0.65 atom p.f.u., compared with the M-type high-temperature exchanged products. The fact that the same sample contained a small amount of residual K^+ ions and its diffraction pattern included a small number of peaks, which could not be indexed in the M-type system, shows that a second phase containing potassium was also formed. Though this phase was not identified, it was deduced from the magnetization of the sample that it has affected the compositional extent of the M-type phase. It was assumed that the extent of the formation of the M phase depends on the Ba content of the sample which is obvious. Anyway, the phenomenon of the phase transition must be attributed to the metastability of the divalent β''-ferrites and not to the procedure of ion exchange itself.

The behavior of the high-temperature Pb-exchange products presented some differences compared with that of Ba or Sr products. An attempt to substitute K^+ with Pb^{2+} at 650°C resulted in the decomposition of the sample to α-Fe_2O_3. When the exchange reaction was performed at a medium temperature, 500°C, the X-ray diffraction pattern was similar to those of the low-temperature exchanged samples (Pb1, Pb2), which represented β phase, but the magnetic behavior was altered. The M(H) curve was of the type $M = M_0 + \chi H$, though no traces of the M-type or another magnetic phase were detected in the X-ray diffraction pattern. The M_{50} value was found to be 22.4 emu/g, which is much less than that of the Ba^{2+} and Sr^{2+} "as exchanged" samples and only 25% that of Pb-M-ferrite. The situation became rather different after annealing of the sample at 1000°C for 24 hr. The β phase disappeared and the X-ray peaks corresponded clearly to those of Pb-M hexagonal ferrite. Traces of α-Fe_2O_3 were also detected. As the K^+ substitution was not 100% (see Table III) it was deduced that regions of K^+-β'' phase, present due to the residual K atoms, decomposed to α-Fe_2O_3 during annealing.

As shown in Table III, the extent of K^+ substitution in Pb3 was less than that of the low-temperature exchanged Pb1 and Pb2 samples, despite the higher temperature used. It was assumed that the use of higher temperature led to an equilibrium between the sample and the binary $PbCl_2$/KCl melt. Such behavior has been also reported by Nariki *et al.* *(40)* who used binary nitrate melts in ion-exchange reactions on K-β-ferrite single crystals with several monovalent ions.

The M_{50} value increased to 72 emu/g, i.e., to ≈84% of Pb-M-ferrite, and the slope of the magnetization curve became considerably lower, as M_{30} differed only 1.5% from M_{50}. The fact that the "as exchanged" sample revealed relative high magnetization compared with the starting K-β''-ferrite material (though the X-ray pattern was similar to that of the low-temperature exchanged Pb1 and Pb2 samples having the β phase) may be due to the formation of ferrimagnetic grains or regions within a grain with the M-type structural arrangement that are too small to be detected by the conventional X-ray powder diffraction method. The superimposed antiferromagnetic component may be due to the domination of the β phase. However, it was clear that the final product, i.e., after annealing, forms an M-type Pb-ferrite as in the cases of Ba and Sr.

b. The case of Mg. In the case of Mg^{2+}, ion exchange at a relatively high temperature, 480°C, resulted in the formation of a spinel-type ferrite (Table III). K^+-ion substitution reached 90% within 1 hr but the inserted Mg atoms exceeded the ratio $K^+ : Mg^{2+} = 2:1$, reaching a value of $\approx 2:3$. Regarding the chemical formula of Mg-spinel ferrite this behavior is expected. X-Ray identification showed that besides the dominating spinel-type structural arrangement, traces of the initial β'' phase were also present. This may be due either to the residual K atoms or to an uncompleted phase transition of the intermediate phase of Mg^{2+}-β''-ferrite.

Magnetization at 50 kOe of the "as exchanged" sample had a value of 34.2 emu/g. After annealing at 1000°C for 24 hr, magnetization increased and M_{50} became 49.4 emu/g. The sample was closer to saturation as M_{30} differed less than 1% from M_{50}, this difference being ≈7% before annealing. The sample reached saturation after annealing above 40 kOe not by means of magnetization stabilization but as a linear increase, indicating the presence of an antiferromagnetic second phase. In fact, traces of the antiferomagnetic α-Fe_2O_3 were detected in the X-ray pattern after annealing. Considering that the diffraction peaks became generally sharper and higher the increase in magnetization could be attributed to the better crystallization of the sample due to the annealing effect.

c. The case of Ca and Cd. Ion exchange with Ca^{2+} and Cd^{2+} at high temperatures, 700 and 600° respectively, led to decomposition of the samples to almost amorphous α-Fe_2O_3. Chemical analysis showed that the entire K content was substituted and the inserted Ca^{2+} or Cd^{2+} ions exceeded slightly the 2 : 1 ratio. In the X-ray patterns, besides α-Fe_2O_3, traces of the β'' phase and of spinel ferrite were observed in the case of Ca and traces of spinel ferrite were observed in the case of Cd. SEM photographs indicated that the microcrystallites were damaged.

3.2.3. Ionic exchange with Co^{2+}, Mn^{2+}, Zn^{2+}, Fe^{2+}, and Sn^{2+}

The attempt to prepare Co^{2+}-, Mn^{2+}-, Zn^{2+}-, Fe^{2+}-, and Sn^{2+}-β''-ferrites was not successful. In the case of Co^{2+} the structure of the initial K^+-β''-ferrite was rearranged to form a spinel-type Co-ferrite. The X-ray pattern of sample Co2 exchanged *in vacuo* at 450°C for 1 hr showed the presence of a small amount of α-Fe_2O_3, which was not the case for the Co1 sample exchanged in argon at 400°C for the same time. The magnetic behavior of both samples was similar to that of sample Mg3. After annealing at 1000°C for 24 hr the X-ray peaks became sharper and more intense and the presence of α-Fe_2O_3 as a secondary phase was clearly observed. The annealed samples were closer to saturation, as M_{30} differed $\approx$10% from M_{50} before annealing but only $\approx$4% afterward. The M_{50} values were 38.4, 65.4 and 42.7, 52.5 before and after annealing for samples Co1 and Co2, respectively. Comparing the sharpness of the diffraction peaks before and after annealing the increase in M_{50} may be due to the better crystallization of the samples during the annealing.

Mn^{2+} and Zn^{2+} exchange products decomposed to α-Fe_2O_3 and the Sn^{2+} product decomposed to an unidentified phase. Potassium substitution reached values between 90 and 100% but the divalent ions' insertion exceeded the 2 : 1 ratio. In the case of Zn^{2+} the inserted Zn^{2+} ions were found to be in the ratio 1 : 2 to the initial K^+ content, as expected from the electrostatic neutrality condition. It is characteristic that in the X-ray pattern of the Zn-exchange product, besides α-Fe_2O_3, traces of spinel-type Zn-ferrite and of the initial β'' phase were detected. It seems that at least Zn^{2+} could be a candidate ion for the corresponding Zn^{2+}-β''-ferrite, but at temperatures lower than that investigated in this work, 280°C.

In the case of Fe^{2+} the powder of K^+-β''-ferrite was chemically attached and, thus, was not able to filtrate the sample. In the X-ray diagram of the frozen melt only peaks corresponding to α-Fe_2O_3 were found. It seems that Fe^{2+} was oxidated to Fe^{3+}, forming α-Fe_2O_3, although the reaction was carried out in an argon atmosphere. Since $FeCl_2$ is very sensitive in such behavior, ionic exchange reactions using $FeCl_2$ must be carried out with great caution.

4. Conclusions

We believe that the experimental results reported in this paper clearly demonstrate that divalent cations diffuse rapidly in β''-ferrite and that ionic exchange with at least six divalent ions on K^+-β''-ferrite lead to the formation of M^{2+}-β''- or M^{2+}-β-ferrites. The main result of this work is that to obtain and retain the β'' structural arrangement, temperatures <500°C must be used. Divalent derivatives of the β'' or β phase seem to be strongly metastable, as they convert to various phases at higher temperatures depending on the inserted cation. We suspect that besides Ba, Sr, Ca, Mg, Cd, and Pb, it will be possible to prepare M^{2+}-β''-ferrites with the other divalent cations investigated in this work (Co^{2+}, Mn^{2+}, Fe^{2+}, Zn^{2+}, and Sn^{2+}), as in the case of the analogous M^{2+}-β''-aluminas, using optimum exchange conditions. Moreover, low-temperature ion-exchange chemistry of divalent cations could be extended to the related K-β-ferrite.

Many questions concerning the properties and applications of the compounds obtained from this work are unexplored. A study of ionic conductivity by means of complex impedance analysis and of thermal stability by means of DTA-TG measurements is in progress and will be published soon (*34*). We also believe that the high-temperature exchange products are of great interest as they lead to modified *M*- or spinel-type ferrites with interesting magnetic properties. It is not clarified whether they consist of single-phase "nonstoichiometric" *M*-type ferrites, as described in (*39*), and spinel-type ferrites or mixtures of different phases. A Mössbauer study of the high-temperature Ba^{2+}- and Sr^{2+}-exchange products is in progress and will be published soon (*41*).

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References

1. G. C. Farrington and J. Briant, *in* "Fast Ion Transport in Solids" (Vashista, Mundy, and Shenoy, Eds.), p. 395, North-Holland, Amsterdam Inc. (1977).
2. S. Sattar, B. Ghosal, M. L. Underwood, H. Mertwoy, M. A. Saltzberg, W. S. Frydrych, G. S. Rohrer, and G. C. Farrington, *J. Solid State Chem.* **65,** 231 (1986).
3. B. Dunn and G. C. Farrington, *Mater. Res. Bull.* **15,** 1773 (1980).
4. G. C. Farrington and B. Dunn, *Solid State Ionics* **7,** 267 (1982).
5. B. Dunn, R. M. Ostrom, R. Seevers, and G. C. Farrington, *Solid State Ionics* **5,** 203 (1981).
6. B. Ghosal, E. A. Mangle, M. R. Topp, B. Dunn, and G. C. Farrington, *Solid State Ionics* **9/10,** 273 (1983).
7. E. E. Hellstrom and R. E. Benner, *Solid State Ionics* **11,** 125 (1983).
8. R. Seevers, J. DeNuzzio, G. C. Farrington, and B. Dunn, *J. Solid State Chem.* **50,** 146 (1983).
9. J. O. Thomas, M. Alden, and G. C. Farrington, *Solid State Ionics* **9/10,** 301 (1983).
10. J. Tegenfeld, M. Underwood, and G. C. Farrington, *Solid State Ionics* **18/19,** 668 (1986).
11. J. D. Barrie, B. Dunn, O. M. Stufsudd, and G. C. Farrington, *Solid State Ionics* **18/19,** 677 (1986).
12. N. J. Dudney and J. B. Bates, *Solid State Ionics* **34,** 53 (1989).
13. G. S. Rohrer and G. C. Farrington, *J. Solid State Chem.* **85,** 299 (1990).
14. S. Nariki, S. Ito, and N. Yoneda, *Bull. Am. Ceram. Soc.* **66,** 1250 (1987).
15. S. Nariki, S. Ito, K. Uchinokura, T. Uchida, and N. Yoneda, *Solid State Ionics* **36,** 103 (1989).
16. O. Kalogirou, D. Samaras, J. Georgiou, and A. C. Stergiou, *Mater. Res. Bull.* **24,** 1399 (1989).
17. H. Vincent, A. Bekka, M. Anne, and J. C. Joubert, *J. Solid State Chem.* **81,** 181 (1989).
18. S. Nicolopoulos, B. Lambert, M. Anne, and H. Vincent, *J. Magn. Magn. Mater.* **89,** 254 (1990).
19. S. Nicolopoulos, H. Vincent, M. Anne, and J. C. Joubert, *J. Solid State Chem.* **87,** 298 (1990).
20. R. C. DeVries and W. L. Roth, *J. Am. Ceram. Soc.* **52,** 364 (1969).
21. J. P. Boilot and J. Thery, *Mater. Res. Bull.* **11,** 407 (1976).
22. S. Nariki, S. Ito, K. Kozawa, T. Uchida, and N. Yoneda, *Solid State Ionics* **40/41,** 95 (1990).
23. S. Ito, N. Kubo, S. Nariki, and N. Yoneda, *J. Am. Ceram. Soc.* **70,** 874 (1987).
24. S. Nariki, S. Ito, K. Uchinocura and N. Yoneda, *J. Cryst. Growth* **85,** 483 (1987).
25. A. Bekka, H. Vincent, S. Nicolopoulos, and J. C. Joubert, *IEEE Trans. Magn.* **MAG-24,** 1844 (1988).
26. O. Kalogirou, A. C. Stergiou, D. Samaras, S. Nicolopoulos, A. Bekka, H. Vincent, and J. C. Joubert, *J. Phys.* **49,** 937 (1988).
27. H. Vincent, A. Bekka, S. Nicolopoulos, M. Anne, J. C. Joubert. O. Kalogirou, D. Samaras, and J. Gonzalez-Calbet, *Cryst. Prop. Prep.* **27–30,** 571 (1989).
28. O. Kalogirou, D. Samaras, and A. C. Stergiou, *J. Magn. Magn. Mater.* **89,** 379 (1990).
29. E. W. Gorter, *Proc. IEEE* **104B,** 225 (1957): *J. Appl. Phys.* **33,** 1253 (1963).
30. T. Takahashi and K. Kuwabara, *J. Solid State Chem.* **29,** 27 (1979).
31. W. Jakubowski and D. H. Whitemore, *J. Am. Ceram. Soc.* **62,** 381 (1979).
32. E. M. Levin, C. R. Robbins, and H. F. McMurdie, *in* "Phase Diagrams for Ceramists" (M. K. Reser, Ed.), 3rd ed., Am. Ceram. Soc., New York (1974).
33. D. Samaras, J. Georgiou, S. Panas, and G. Litsardakis, *IEEE Trans. Magn.* **MAG-26,** 18 (1990).
34. O. Kalogirou, E. Sanchez, G. Bonsdorf, and W. Gunsser, to be published.

35. J. B. Bates, J. C. Wang, N. J. Dudney and W. E. Brundage, *Solid State Ionics* **9/10,** 237 (1983).
36. J. Carbarczyk, W. Jakubowski, and M. Wasiucionek, *Solid State Ionics* **9/10,** 249 (1983).
37. M. Alden, J. O. Thomas, and G. C. Farrington, *Solid State Ionics* **5,** 205 (1981).
38. T. Fujiwara, *IEEE Trans. Magn.* **MAG-21,** 1480 (1985).
39. A. C. Stergiou, D. Samaras, O. Kalogirou, H. Vincent, and A. Bekka, *Solid State Ionics* **50,** 11 (1992).
40. S. Nariki, S. Ito, K. Uchinokura, and N. Yoneda, *J. Electrochem. Soc.* **136,** 2093 (1989).
41. O. Kalogirou, G. Haack, B. R. Roehl, and W. Gunsser, 12th International Conference on the Reactivity of Solids, contr. C-31, Madrid 1992.