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(β-$NaFeO_2$)$_{1-x}$(SiO_2, GeO_2)$_x$ Solid Solutions: A Study by X-ray Diffraction, IR Spectroscopy, and Ionic Conductivity Measurements

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An extended series of solid solutions $(NaFeO_2)_{1-x}(SiO_2$ or $GeO_2)_x$ may be obtained in the composition range $0 < x \leq 0.327$. They result from the isomorphic replacement $Na^+Fe^{3+} \rightarrow \square Si^{4+}$. Three families of solid solutions have been evidenced: ϕ_1 for $0 \leq x \leq 0.14$, with the β-$NaFeO_2$ structure; ϕ_2 for $0.12 \leq x \leq 0.25$ derived from the preceding structure by doubling two of the three orthorhombic axes; ϕ_3 (whose precise composition is still to be determined: it is obtained in admixture with Fe_2O_3) for $0.27 \leq x \leq 0.327$, cubic. The strong structural analogy between ϕ_1 and ϕ_2 has been established in recently published X-ray diffraction studies. Infrared spectra are presented and discussed in relation with the structure. Electric conductivity measurements show that the solid solutions with $0.10 \leq x \leq 0.20$ are reasonably good Na^+ ionic conductors at 600 K.

Introduction

Besides well-reproducible absorption bands, the IR spectrum of β-$NaFeO_2$ synthesized by solid state reaction between Fe_2O_3 and $NaHCO_3$ exhibits near 900 cm^{-1} a weak doublet whose intensity depends on the origin of the Fe_2O_3 used in the synthesis. This doublet disappears completely if commercial Fe_2O_3 is replaced by a very pure compound (e.g., obtained by heating iron(II) oxalate at about 600°C). In view of the position and shape of these spurious bands, and since β-$NaFeO_2$ is a tetrahedral structure (*1*), we suspected SiO_2 as a possible impurity entering in the β-$NaFeO_2$ structure as SiO_4 tetrahedra replacing FeO_4 tetrahedra. We have accordingly investigated the formation of solid solutions (β-$NaFeO_2$)$_{1-x}$(SiO_2 or GeO_2)$_x$. When our work was completed, we became aware of two papers by Grey and co-workers describing the system $NaFeO_2$–SiO_2 (*2*) and presenting a detailed structural study of two of the solid solutions appearing in this system (*3*).

Experimental

Synthesis of the Samples

Classical techniques of solid state chemistry have been used throughout. The stoichiometric quantities of pure $NaHCO_3$, Fe_2O_3, and SiO_2 (aerosil) or GeO_2 are well ground and mixed, and progressively

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heated in platinum crucibles up to a final temperature of 700–900°C (depending on the chemical composition). This temperature is maintained with intervening mixing and grinding as long as no modification is observed in the X-ray powder diagram (generally 1 to 3 days).

X-ray Diffraction

The X-ray powder diagrams have been obtained with a C.G.R. diffractometer (Co$K\alpha$ radiation; Si as an internal standard for some samples).

Infrared Spectroscopy

The IR spectra have been registered with a Beckman 4250 spectrophotometer (1400–300 cm^{-1} region, KBr discs) and a Polytec FIR 30 interferometer (350–30 cm^{-1} region, polyethylene discs). Some spectra were also run in NaCl discs or Nujol mulls, in order to check the lack of ionic exchange in KBr discs.

Ionic Conductivity

The powdered samples are cold-pressed into discs (diameter 18 mm, thickness about 1.2 mm) which are then progressively heated up to the synthesis temperature. Silver paint is applied to the faces, and the electric conductivity is measured with a Hewlett–Packard 4192 A impedancemeter by the complex impedance method. The reliability of this technique has been discussed in a recent paper (*4*).

Results

X-ray Diffraction

Three types of phases, labeled ϕ_1, ϕ_2, and ϕ_3, have been obtained in the system $(\text{NaFeO}_2)_{1-x}(\text{SiO}_2 \text{ or } \text{GeO}_2)_x$ as a function of composition (x value) and, to a lesser extent, of temperature. These phases are labeled β, γ', and δ, respectively, in Ref. (*2*).

Phase ϕ_1. This phase exhibits all the diffraction peaks of β-NaFeO_2 itself, without additional peaks, but with a continuous variation of the d values when the percentage of SiO_2 (or GeO_2) increases. As pointed out in (*2*), it is thus a solid solution with the orthorhombic β-NaFeO_2 structure (*5*). It is observed in the composition range $0 \leq x \leq 0.11$, whatever the synthesis temperature (750–900°C), and also for $0.12 \leq x \leq 0.14$ if the synthesis temperature is high enough (850–900°C) (for these latter compositions and at lower temperature, e.g., 750°C, ϕ_2 is formed; see below).

This latter point is at variance with the results presented in (*2*), according to which, for a given composition such as $x = 0.11$, ϕ_2 is formed at high temperature, whereas ϕ_1 is recovered after cooling at room temperature. A possible explanation of these discrepancies will be presented under the heading Discussion.

The variations of the unit cell parameters are clearly anisotropic, in agreement with (*2*). A nearly similar behavior is observed for the GeO_2-bearing solid solutions, but with slightly larger values of the unit cell parameters (Fig. 1). In both cases, the overall effect is a significant decrease of the unit cell volume. If we admit that Si(or Ge) replaces Fe in the structure, this is consistent with the ionic radii of these cations for tetrahedral coordination (0.26, 0.39, and 0.49 Å for Si, Ge, and Fe, respectively) (*6*).

Phase ϕ_2. We have already noted that, for the solid solutions with $0.12 \leq x \leq 0.14$ annealed at 750°C, the phase ϕ_1 disappears and is replaced by another phase ϕ_2. This second phase is also obtained at about 850–900°C for all the compositions within the range $0.15 \leq x \leq 0.25$, independently from the nature of the substituting oxide (either SiO_2 or GeO_2). Phase ϕ_1 has never been obtained in this last composition range.

Our X-ray powder diffraction data and their indexation are in agreement with those already published by Grey and Li (*2*): the orthorhombic unit cell is deduced from that of ϕ_1 by doubling two of the three axes.

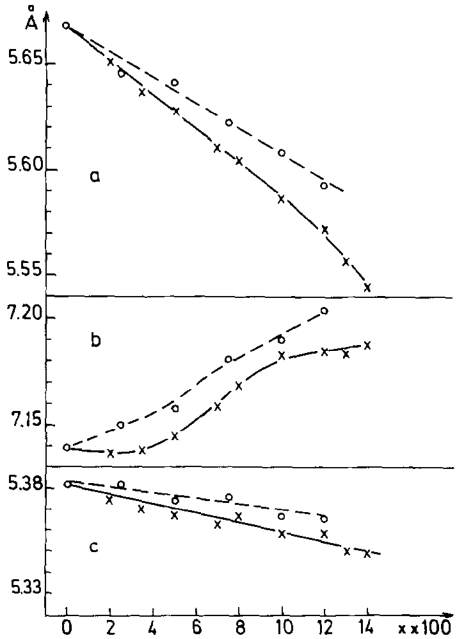

FIG. 1. Relationships between the composition and the unit cells parameters for ϕ_1-type solid solutions. Circles: $(NaFeO_2)_{1-x}(GeO_2)_x$; crosses $(NaFeO_2)_{1-x}(SiO_2)_x$.

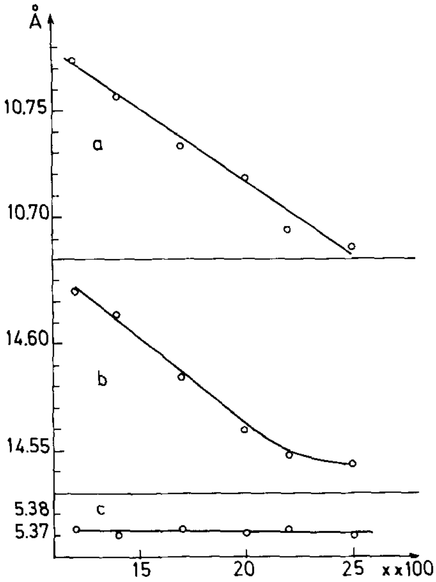

FIG. 2. Relationships between the composition and the unit cell parameters for ϕ_2-type solid solutions $(NaFeO_2)_{1-x}(SiO_2)_x$.

These two large axes decrease fairly regularly when increasing the substitution rate, whereas the third (the smallest) one remains nearly constant (Fig. 2). Three solid solutions with GeO_2 ($x = 0.15$, 0.20, and 0.25) have also been synthesized. As expected, the unit cell parameters are slightly larger than the corresponding parameters of the SiO_2-containing solid solutions.

Phase ϕ_3. For $0.27 \leq x \leq 0.327$, the X-ray powder diagrams exhibit a new series of peaks, some of which are clearly due to α-Fe_2O_3. The series of the remaining peaks is characterized by the following features:

—The two strongest peaks are observed at d values very similar to those already noticed for the ϕ_1 and ϕ_2 phases.

—The whole series is readily interpreted by a cubic cell with $a \approx 7.45$ Å (somewhat depending on composition), to be compared with the value of the b axis of ϕ_1 (Table I). These features strongly suggest the existence of a third phase ϕ_3 structurally related to ϕ_1 and ϕ_2.

The same phase has also been observed (but free from Fe_2O_3) by Grey and Li (2),

TABLE I

INDEXATION FOR $(NaFeO_2)_{0.68}(SiO_2)_{0.32}$ SOLID SOLUTION (ϕ_3)

d_{obs}	d_{calc}[a]	hkl	I
4.3034	4.3019	111	80
2.6335	2.6344	220	100
2.2461	2.2466	311	3
2.1502	2.1509	222	2
1.8633	1.8628	400	14
1.7097	1.7094	331	5
1.5212	1.5209	422	25
1.4341	1.4340	511 333	5
1.3173	1.3172	440	4
1.1780	1.1781	620	5

[a] For $a = 7.4511$ Å.

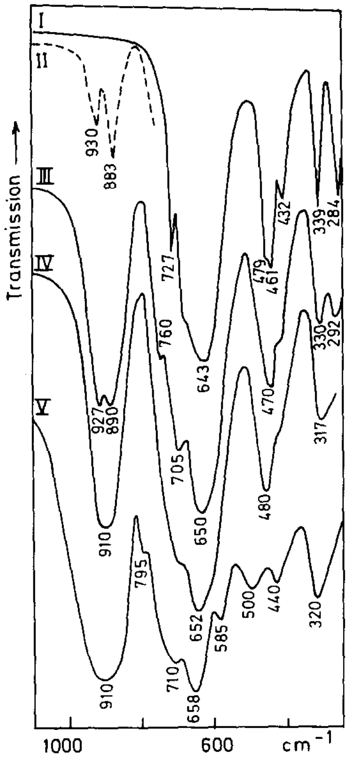

FIG. 3. IR spectra of $(\text{NaFeO}_2)_{1-x}(\text{SiO}_2)_x$ solid solutions in the 1000–280 cm^{-1} region: I, pure β-NaFeO_2 and II(dashed), additional bands due to SiO_4 tetrahedra for $x = 0.02$; III and IV, $x = 0.13$ for the two polymorphs ϕ_1 (III) and ϕ_2 (IV); V: $x = 0.25$ (ϕ_2).

even for much smaller x values (in fact, down to $x = 0$, for pure NaFeO_2); but in this composition range, this cubic phase is not quenchable and must be investigated by high-temperature X-ray diffraction.

In our experiments, the formation of ϕ_3 is observed for x values up to 0.327 (though this last composition is characterized by a significant broadening of the diffraction peaks); but ϕ_3 is no longer present for $x = 0.334$: X-ray diffraction (and also IR spectroscopy) shows a mixture of Na_2SiO_3 and Fe_2O_3, formed according to the reaction $2\text{NaFeO}_2 + \text{SiO}_2 \rightarrow \text{Na}_2\text{SiO}_3 + \text{Fe}_2\text{O}_3$. Thus, there is a very sharp break in the behavior of the system $\text{NaFeO}_2 + \text{SiO}_2$ when the Na/Si ratio is equal to two, and thus when there is no Na^+ excess with respect to the stoichiometric quantity required to form Na_2SiO_3.

Infrared Spectra

Representative spectra of pure β-NaFeO_2 and solid solutions are given in Figs. 3 and 4. For this type of structure (a 3-D lattice of FeO_4 tetrahedra, or FeO_4–SiO_4 tetrahedra in the solid solutions), it is impossible to propose a detailed assignment of all the observed frequencies. But if we consider absorption *regions* (and not the detail of the individual frequencies), we see (Figs. 3 and 4) that four absorption regions are common to all compositions, namely, 700–600, 500–400, near 300, and near 200 cm^{-1}.

According to infrared spectra registered in this laboratory, other compounds with a 3-D lattice of FeO_4 tetrahedra (such as

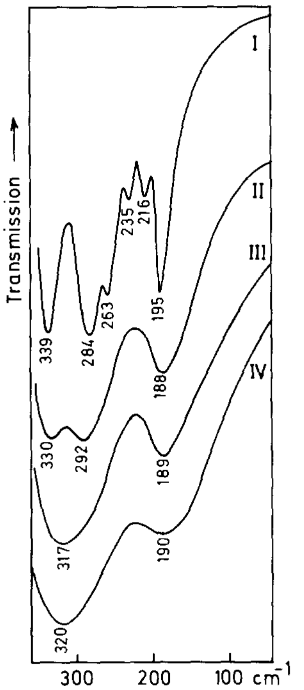

FIG. 4. IR spectra of $(\text{NaFeO}_2)_{1-x}(\text{SiO}_2)_x$ solid solutions in the low-frequency region: I, pure β-NaFeO_2; II and III, $x = 0.13$ for the two polymorphs ϕ_1 (II) and ϕ_2 (III); IV, $x = 0.25$ (ϕ_2).

$BaFe_2O_4$, or $BaSrFe_4O_8$ with a stuffed tridymite structure (*7*) exhibit three absorption regions which are very similar to those already observed in β-$NaFeO_2$ (though the number and frequencies of individual bands are somewhat different from compound to compound), namely 700–600, 500–400, and near 300 cm^{-1}.

The highest frequency region is certainly due to stretching motions of the lattice of FeO_4 tetrahedra; the other absorptions are tentatively assigned, either to motions with a mixed stretching–bending character (500–400 cm^{-1}) or to essentially bending vibrations (near 300 cm^{-1}). The remaining absorption near 200 cm^{-1} is probably due to a translational motion of the Na^+ cation.

For the SiO_2-bearing solid solutions, the most characteristic feature of the IR spectrum is the doublet near 900 cm^{-1} (missing in the spectrum of pure $NaFeO_2$), whose relative intensity increases with the SiO_2 percentage; there is a simultaneous increase of the broadness of the bands (the components of the doublet are only weakly separated for $x = 0.13$; Fig. 3).

A comparison with the IR spectra of a number of silicates, or silicate-bearing solid solutions (*8*), shows that this doublet must be assigned to the degenerate antisymmetric stretch ($\tilde{\nu}_3$) of an "isolated" SiO_4 tetrahedron in the pseudo-tetragonal lattice of β-$NaFeO_2$. For small x values (e.g., 0.01 or so), the average distance between SiO_4 tetrahedra is large, vibrational interactions are small to negligible, and the bands are sharp; with increasing x values, the average SiO_4–SiO_4 distance decreases, and the broadness of the bands increases as a result of increasing vibrational interactions.

A definite proof of the origin of these bands is given by the existence of a ^{28}Si–^{30}Si isotopic shift. For $x = 0.01$, the bands are observed at 930 and 883 cm^{-1} for natural SiO_2 (essentially ^{28}Si), but they are shifted to 920 and 876 cm^{-1} for $^{30}SiO_2$.

The IR spectra of the ϕ_1- and ϕ_2-type solid solutions are very similar (Fig. 3 and 4). Small differences appear in the 900 and 300 cm^{-1} regions, where the doublet observed in the ϕ_1-type solid solutions is replaced by a single broad band. But apart from the 500–450 cm^{-1} region, where the spectrum is somewhat modified for high x values (this can be explained by a contribution of the (SiO_4) bending vibrations), the overall pattern remains the same, indicating that no gross modification has occurred in the coordination of the cations. This is in agreement with the structural analogies evidenced for these two phases (*3*).

The vibrational behavior of the GeO_2-bearing solid solutions does not fit this scheme: the stretching frequencies of GeO_4 and FeO_4 tetrahedra are not very different, thus leading to strong vibrational interactions which preclude the existence of localized modes characteristic of "isolated" GeO_4 tetrahedra.

Electric Conductivity

For all investigated phases, the electric conductivity obeys an Arrhenius-type relationship $\sigma T = Ae^{-E_a/RT}$. This result, together with the increase of conductivity as a function of frequency, shows that this conductivity is essentially of ionic origin. The behavior is essentially the same for the SiO_2- or GeO_2-bearing solid solutions, but depends on the x values. For increasing values of x, we observe successively (Table II and Fig. 5):

TABLE II

Ionic Conductivity Data

		$\sigma(\Omega^{-1}cm^{-1})$	
Composition	E_a (kJ/mole)	600 K	400 K
β-$NaFeO_2$	49.5	9.9×10^{-4}	1.1×10^{-5}
$(NaFeO_2)_{0.9}(GeO_2)_{0.1}$	39.5	5.2×10^{-3}	1.5×10^{-4}
$(NaFeO_2)_{0.9}(SiO_2)_{0.1}$	38.5	2.7×10^{-3}	8.8×10^{-5}
$(NaFeO_2)_{0.85}(GeO_2)_{0.15}$	45	1.0×10^{-2}	1.6×10^{-4}
$(NaFeO_2)_{0.85}(SiO_2)_{0.15}$	40	5.8×10^{-3}	1.6×10^{-4}
$(NaFeO_2)_{0.8}(GeO_2)_{0.2}$	47	4.9×10^{-3}	6.7×10^{-5}
$(NaFeO_2)_{0.8}(SiO_2)_{0.2}$	45.5	5.8×10^{-3}	9.1×10^{-5}

—between $x = 0$ and 0.1 (phase ϕ_1), a decrease of the activation energy and an increase of the electric conductivity. This is probably related to the formation of Na^+ vacancies associated to the NaFe → Si replacement.

—between 0.1 and 0.15 ($\phi_1 \rightarrow \phi_2$), a small increase of both activation energy and conductivity. It is hard to decide whether these small variations are significant or not, due to the errors involved in this type of experiments (*4*).

—between 0.15 and 0.20 (ϕ_2), small, possibly non-significant variations of both activation energy and conductivity. According to the results obtained at 600 K (Table II), these solid solutions are reasonably good Na^+ ionic conductors.

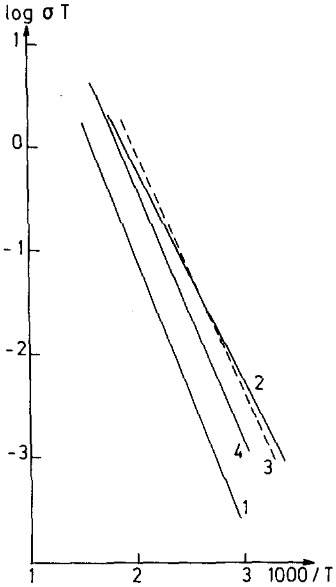

FIG. 5. Influence of temperature on the ionic conductivity of β-$NaFeO_2$ (1) and $(NaFeO_2)_{1-x}(GeO_2)_x$ solid solutions (2, 3, and 4 for $x = 0.10$, 0.15, and 0.20, respectively). σ is expressed in $ohm^{-1}cm^{-1}$; T in Kelvin.

Discussion

Relative Stabilities of the ϕ_1 and ϕ_2 Phases

The structures of the ϕ_1- and ϕ_2-type solid solutions have been recently determined by Rietveld refinements of X-ray powder intensity data. With respect to the structure of β-$NaFeO_2$ itself, the structural modifications involve, first a rotation of the FeO_4 (SiO_4) tetrahedra, and, in ϕ_2, a partial ordering Fe/Si and Na/□ in the tetrahedral framework (*3*).

As pointed out earlier in this paper, an apparent point of disagreement is the relative stability (as a function of temperature) of the phases ϕ_1 and ϕ_2. According to (*2*), either ϕ_1 or ϕ_2 may be obtained in the composition range $0.07 \leq x \leq 0.125$, where ϕ_2 is the high-temperature phase. We find an opposite behavior in the composition range $0.12 \leq x \leq 0.14$, with ϕ_1 as the high-temperature phase (quenchable from 900°C), whereas ϕ_2 appears at about 750–700°C and below. The transformation is fully reversible, although not very rapid (no signal observed by DTA). For $x > 0.14$, only ϕ_2 is obtained, in agreement with (*2*). Our findings are consistent with the fact that, for a given x value (0.12, 0.13, or 0.14), the molar volume is slightly but systematically smaller for ϕ_2 than for ϕ_1 (the difference is small, about 1%, but well reproducible). Likewise, since the ϕ_2-type solid solutions are characterized by partial ordering phenomena, they are expected to be the low-temperature polymorph.

In fact, the whole series of experimental results can be explained if we consider a stabilizing influence of the Fe/Si and Na/□ ordering on the ϕ_2-type solid solutions. For small x values, the amount of ordering is necessarily small, and ϕ_1 remains the phase stable at room temperature. But for higher and higher substitution rates (and thus amounts of ordering) the situation is eventually reversed: ϕ_2 becomes the low-temperature phase and finally remains the only phase observed (for $0.15 \leq x \leq 0.25$).

Influence of the $\phi_1 \rightarrow \phi_2$ Transition on the Broadness of the Infrared Bands

Since the ϕ_2 phase is characterized by a partial ordering of Fe/Si and Na/□ cations and vacancies, one could expect some sharpening of the IR bands, but the experimental results (Figs. 3 and 4) do not support this expectation. In fact, no full ordering is possible, because of the variable stoichiometry of these solid solutions, and the influence of a partial ordering is overcome by the remaining disorder. The influence of an order–disorder competition on the vibrational spectrum of a solid has been discussed in a recent review paper (*9*).

Similar Replacements in Other Host Lattices

The substitution scheme reported in this paper, namely $Na^+Fe^{3+} \rightarrow \square Si^{4+}$, should be applicable to other compounds, provided the trivalent cation is tetrahedrally coordinated. We have carried out a few exploratory experiments limited to a small replacement rate (1 mole%), the formation of a solid solution being easily evidenced by the peculiar shape of the SiO_4 infrared bands. Infrared bands typical for the SiO_4 tetrahedron in dilute solid solutions are observed for the host compounds $Na_3Fe_5O_9$, $NaAlO_2$, $NaGaO_2$, $LiAlO_2$, and $LiGaO_2$. No replacement could be evidenced in $LiAl_5O_8$ or $LiFe_5O_8$ with spinel structure.

The formation of solid solutions is also observed with ferrites of divalent cations, such as $BaFe_2O_4$, $CaBaFe_4O_8$, and $Ca_2Fe_2O_5$. It is concluded that much additional work can be carried out in this field.

Acknowledgments

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