JOURNAL OF SOLID STATE CHEMISTRY **91,** 71–81 (1991)

Structural Refinements on a Sodium β-Aluminogallate Crystal and a Parent Nd^{3+}-Exchanged Crystal

A. KAHN-HARARI,* G. AKA, AND J. THÉRY

C.N.R.S., URA 302, Chimie de la matière condensée, Laboratoire de chimie appliquée de l'état solide, E.N.S.C.P., 11 rue P. et M. Curie, 75231 Paris cedex 05-France

Received June 13, 1990; in revised form October 8, 1990

X ray structural refinements are performed on a sodium β-aluminogallate single crystal and on the corresponding Nd^{3+}-exchanged compound, which presents potential laser applications. In the hexagonal unit cells ($a = b = 5.667$ Å, $c = 22.663$ Å, $Z = 2$ for the Na^+ compound and $a = b = 5.644$, $c = 22.610$ Å for the Nd-exchanged compound), the study of ion distribution reveals a single position for the rare-earth active ion, a highly disordered distribution of sodium ions in the mirror-planes of the structure and a nonrandom localization of gallium in the available sites.

Introduction

In recent years, the fast-ionic conductor Na^+ β-alumina has been extensively studied for its ability for ionic exchange, which allows the incorporation of quite a variety of monovalent and divalent ions (*1–3*). The search for insertion of transition metal or lanthanide ions was of great interest in order to add optical properties to the well known electrical ones.

The parent structural type, β″-alumina, with the same kind of open structure, already appears as an exciting host lattice, of great spectroscopic interest, with Nd^{3+}, Ce^{3+}, and Pr^{3+} ions (*4, 5*). In β-alumina however, insertion of large rare earth ions is not possible, probably due to the more rigid stacking of the lattice. Therefore, sodium aluminogallate solid solutions with the same β-alumina structure have been studied and appear to be very attractive host materials (*6*). They are able to welcome not only divalent but also trivalent ions by ionic exchange in molten salts. Several features are encouraging for further studies:

—Crystal growth of Na β-aluminogallate is convenient and optical properties of doped materials are already promising (*7*).

—The lattice constants can be modified by varying the Al : Ga ratio.

—The presence of Ga lowers the crystal field around the optically active ion.

As the starting material determines the ion exchange potentialities, an X ray structural investigation of Na β-aluminogallate was undertaken. A comprehensive structural description of this compound should greatly help in the understanding of exchange reactions. A tentative description of a Nd partially exchanged crystal structure is proposed in the second part.

---

* To whom correspondence should be addressed.

0022-4596/91 $3.00

TABLE I

CRYSTALLOGRAPHIC DATA AND PROCEDURE

$Na_{1+x}(Al, Ga)_{11}O_{17+x/2}$	β-alumina type	(Na, Nd)(Al, Ga)$_{11}$O$_{17}$	β-alumina type
Crystal symmetry	hexagonal	Crystal symmetry	hexagonal
Space group	$P6_3/mmc$ Z= 2	Space group	$P6_3/mmc$ Z= 2
Unit cell		Unit cell	
$a = b = 5.667$ Å		$a = b = 5.644$ Å	
$c = 22.663(1)$ Å	$\gamma = 120°$	$c = 22.610(1)$ Å	$\gamma = 120°$
$c/a = 3.99$	$V = 630.3$ Å^3	$c/a = 4.0$	$V = 623.7$ Å^3
Density	$\rho_{th} = 3.98$	Density	$\rho_{th} = 4.10$
Crystal size	0.3 × 0.4 × 0.17 mm	Crystal size	0.2 × 0.3 × 0.05 mm
Linear absorption coefficient	$\mu = 81$ cm^{-1}	Linear absorption coefficient	$\mu = 90$ cm^{-1}
Data collection Nonius CAD4 diffractomoeter			
$\lambda MoK\alpha = 0.7107$ Å			
Graphite monochromator			
Theta/omega scan scanning speed: 1.5 to 6.7°/min			
$0 < h < 10$ $0 < k < 10$ $0 < l < 42$		$0 < h < 10$ $0 < k < 10$ $0 < l < 40$	
$\sin \theta/\lambda_{max} = 0.95$		$\theta_{max} = 42.0°$	
902 independent reflections of which 192 were unobserved with $I < 3\ \sigma$		1354 independent reflections of which 359 unobserved with $I < 3\sigma$	
Ion scattering factors: International Tables for Cryst., Vol. IV			
R factor on $\lvert F(hkl)\rvert$ 0.029		R factor on $\lvert F(hkl)\rvert$ 0.049	
with 567 reflections ($F > F_{max}/20$)		with 535 independent reflections ($F > F_{max}/20$)	
2 or 3 Na sites		2 Na sites, 1Nd site	
No improvement with extinction correction			

Structural Investigation of Na β-Aluminogallate

Experimental

Large single crystals were grown, for several Al/Ga ratios, by a flux evaporation method, using a mixture of sodium fluoride and polycrystalline sodium aluminogallate heated at 1450°C. Experimental conditions are described elsewhere (*6*). Electron microprobe analysis of such prepared selection of crystals provided a composition: $Na_{1+x}(Al_{1-y}Ga_y)_{11}O_{17+x/2}$ with a high sodium rate, $x = 0.7$. In these crystals, the total Al/Ga ratio was about 7.7/3.3.

Intensity measurements were performed at room temperature, on a crystal having dimensions 0.17 × 0.33 × 0.4 mm. All experimental data are presented in Table I. No diffuse scattering was detected on this crystal, so the "mean" structure was refined with the $P6_3/mmc$ space group, which had been previously assigned for similar compounds with β-alumina type structure.

Let us recall that β-alumina consists of spinel-like blocks, $Al_{11}O_{16}$, separated by loosely packed planes in which are found the mobile sodium ions. These are occupying several sites statistically, with a dynamic disorder, leading to an apparent partial occupancy of several Wyckoff positions and very high temperature factors (*8*). As the compound contains an excess of Na^+ ions, these charges have to be balanced by some excess oxygen, the location of which has been evidenced previously in basic β-alumina (*9*).

Refinement and Description of the Structure

This crystal structure was refined in the $P6_3/mmc$ space group, using as initial

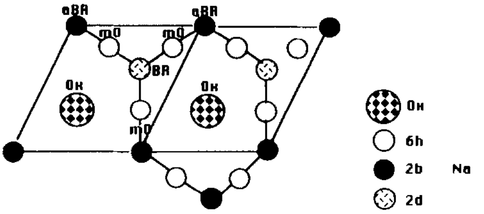

FIG. 1. Sodium conduction sublattice in Na^+ β-aluminate or -gallate.

atomic coordinates those of basic sodium β-alumina (*8*). Scattering factors were taken for fully ionized ions from "International Tables for X Ray Crystallography" (*10*).

The main purposes of this investigation were:

—to characterize the nonstoichiometry,

—to determine the exact distribution of gallium and aluminum on the available sites of the structure.

Therefore particular attention was set on occupancy and thermal factors, keeping in mind that minimizing the R factor is not the only criterion of good fit, since the resulting values should keep a physical meaning.

Successive steps of refinement were performed with a VAX private adaptation of Busing and Levy's OXFLS routine. No weighting scheme was applied but very weak reflections with $F_{hkl} < F_{max}/20$ were neglected (together with two very intense reflections with high primary extinction such as 2,4,0). The refinement led to well-defined atomic coordinates with variations less than 1/10 of the error. Further refinement of occupancy factors allowed a tentative assignment of gallium/aluminum distribution on the four sites available for these atoms.

Afterwards anisotropic temperature factors were introduced for the atoms of the mirror planes which exhibited very high vibrational amplitudes. Sodium appeared to be highly disordered on several partially occupied positions, as it is in sodium β-alumina. Several assignments were tried, involving either two or three different sites for the sodium ion, with no significant improvement of the R agreement factor: this clearly shows the dynamic disorder of Na^+ ions, which are in fact not localized on their available positions, building the conduction sublattice (Fig. 1)

The final set of atomic parameters corresponding to an agreement factor $R = 0.029$, is given in Table II. The temperature factors are in Table III and the distribution of

TABLE II

FINAL SET OF ATOMIC COORDINATES IN Na^+ β-Aluminogallate ($R = 0.029$)

Type of atom	Wyckoff position	Coordination polyhedra	Coordinates x	y	z	Thermal isotropic B coefficient
$M1$ Al	2a	Octahedron	0	0	0	0.24
$M3$ Ga	4f	Tetrahedron	0.3334	0.6667	0.0248(0)	0.33
$M4$ 0.3 Ga + 0.7 Al	4f	Tetrahedron	0.3334	0.6667	0.1758(1)	0.35
$M5$ 0.2 Ga + 0.8 Al	12k	Octahedron	−0.1676(1)	−0.3353	0.1079(0)	0.38
M_{int} Al	12k	Tetrahedron	−0.1667	−0.3334	0.1745(0)	0.10
O1	4e		0	0	0.1441(2)	0.52
O2	4f		0.6667	0.3334	0.0573(2)	0.41
O3	6h		0.3023(27)	0.6045	0.250 (0)	3.60
O4	12k		0.1531(3)	0.3062	0.0511(1)	0.44
O5	12k		0.5038(4)	0.0076	0.1475(1)	0.56
Na (BR) 0.72/plane	2d		0.6667	0.3334	0.250	12.0
Na (mO) 0.63/plane	6h		0.9003(30)	0.8006	0.250	10.0
Na or O_{int} 0.12/plane	6h		0.7703(27)	0.5405	0.250	1.0

TABLE III

Mean Square Amplitudes of Vibrations ($\times 10^5$ Å^2) for Atoms in the Conduction Plane and Equivalent Isotropic Thermal Factors for Na Aluminogallate

Atomic site	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	Beq
Na1 (2d)	2258	2258	260	1129	0	0	12.0
Na2 (6h)	1151	2600	130	1300	0	0	10.0
Na3 or O (6h)							1.0
O3 (6h)	462	452	52	226	0	0	3.6

ions leading to the refined composition is presented in Table IV.

The main features of the structure are as follows:

—Gallium atoms are mainly found on both tetrahedral sites (4f Wyckoff positions) as expected from previous study of similar compounds, with predominance on the tetrahedron located in the middle of the spinel blocks (*11*). A small amount is also located in the octahedral site 12k.

—Sodium is more difficult to localize (Fig. 2). One solution consists of 2 Na$^+$ positions, partially occupied, one on a fixed 2d site (so-called BR), and one near the 2b position (aBR site), which gives a more reasonable thermal factor than a mO(6h) location. A tentative set of three sodium ions close to BR, mO, aBR sites does not result in a better description of the "true" situation, but it still looks like a good way to account for the high amplitudes of vibration of sodium ions.

—The very strong correlations between positions and vibration amplitudes are the predominant limiting factor for a correct assignment of ion positions in the mirror planes of the structure.

—The total amount is about 1.47(Na + interstitial oxygen) per plane. As generally admitted in β-alumina type of compounds, the presence of more than one Na$^+$ per plane requires an excess of oxygen for the charge balance; these supplementary oxygens are expected to be in the "mO" 6h positions of Na. As Na$^+$ and O^{2-} are isoelectronic, they cannot be discriminated by X-Ray investigation, especially in nonstoi-

TABLE IV

Actual Occupancy of Cationic Sites in Na β-Aluminogallate

Type of site	Multiplicity		Nb per site	Occupancy		
	Theoretical	Refined		Ga	Al	Na
Al1 *2a* octahedral	0.083	0.099	1.19	0.10	0.90	
Ga3 *4f* tetrahedral	0.167	0.163	0.98	0.97	0.03	
Al4 *4f* tetrahedral	0.167	0.26	1.55	0.33	0.67	
Al5 *12k* octahedral	0.5	0.664	0.34	0.19	0.81	
Na1 *2d*	0.083	0.060	0.72			
Na2 *6h*	0	0.052	0.63/3			$\Sigma = 1.47$
Na3 *6h*	0	0.010	0.12/3			

Note. Composition: $Na_{1.32}Al_{7.2}Ga_{3.8}O_{17.16}$.

chiometric compounds. Therefore, it is difficult to detect interstitial oxygen in the mirror-planes of the structure to balance the sodium excess. However, small amounts of aluminum (or gallium) are detected on an interstitial site (difference Fourier map) and this corresponds to the occurrence of the well-known Frenkel defect of β-alumina, assuming the existence of interstitial oxygen in the mirror plane on the 6h mO positions (9).

The difference Fourier map exhibits values of residual electron density for the final set of coordinates, corresponding to 1.9 electron/Å^3, located on position 0, 0, $\frac{1}{4}$.

The final distribution of ions leads to the refined composition $Na_{1.33}Al_{7.2}Ga_{3.8}O_{17.16}$ (the total of Na + O_{int} is 1.47 atom per plane; as xNa in excess are balanced by $x/2$ oxygen, this corresponds to 1 + 0.32 Na and 0.16 O in excess, from which is drawn the final composition here above).

This formula differs from the composition determined by electron microprobe analysis, on the batch of crystals where the studied sample comes from. In both cases, the methods have inherent systematic errors which leave some uncertainty on the true composition. Some extra sodium could have been found outside of the crystals in the crystal bulk on which the EPMA was performed. However, the ratio Al/Ga has the same magnitude in both evaluations.

The main difference due to the presence of gallium in this β-alumina structure lies in the larger bond lengths (Table V) apart from the mirror-planes, and results from the presence of a certain amount of gallium in the tetrahedra close to the conduction planes (Fig. 3). The sodium ion in this environment is probably less constrained within the mirror plane, and it can be easily exchanged by a rare earth ion, which was not possible in pure Na β-aluminate.

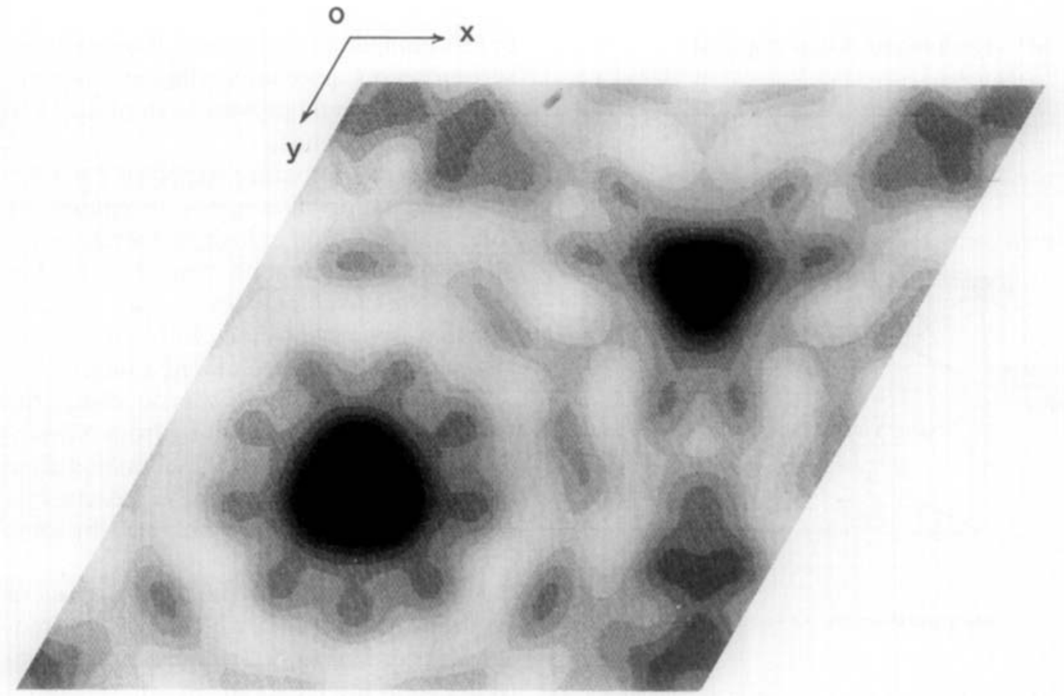

FIG. 2. Electron density map in the mirror-plane (z = 0.25) of Na^+ β-aluminogallate.

TABLE V

MAIN INTERATOMIC DISTANCES IN Na^+ Aluminogallate

Atomic site	Coordination number	M–O bond-lengths in Na compound		Type of atom
M1(2a)	6	6 × O4	1.897(3)	0.1 Ga + 0.9 Al
M3(4f)	4	3 × O4	1.858(4)	Ga
		1 × O2	1.868(3)	
M4(4f)	4	1 × O5	1.714(4)	0.33 Ga + 0.67 Al
		3 × O3	1.792(3)	
M5(12k)	6	1 × O1	1.839(3)	0.19 Ga + 0.81 Al
		2 × O5	1.845(2)	
		1 × O2	1.992(2)	
		2 × O4	2.036(2)	
M_{int}(12k)	4	O1	1.683(20)	Al
		2 × O5	1.808(20)	
		O3	2.217(30)	
Na1(2d)	9	6 × O5	2.823(2)	
		3 × O3	3.12(1)	
Na2(6h)	9	2 × O1	2.59(1)	
		3 × O3	2.62(2)–2.99(2)–3.13(2)	
		4 × O5	3.09(1)	
Na3(6h) or Ox int	9	2 × O1	3.29(3)	
		3 × O3	2.69(7)–2.85(7)–3.18(6)	
		4 × O5	2.71(3)	

Nd^{3+}-Exchanged Aluminogallate

Ionic exchange has been performed in this Na^+ β-aluminogallate, leading to more or less complete substitution. Rare earth insertion seems quite interesting in this compound, for it could provide both optical and electrical properties.

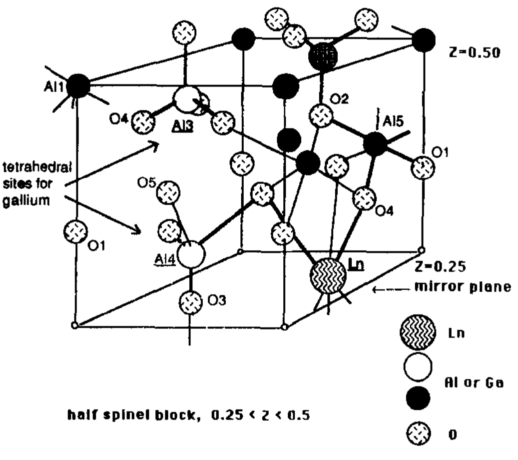

FIG. 3. Localization of gallium in the aluminogallate lattice.

The normal structure expected for Ln^{3+} hexagallates or aluminates, prepared by solid state reaction at high temperatures, is of the magnetoplumbite type (*11–14*). For mixed Na/Ln aluminates, a new type of stacking was established, with alternate β-alumina and magnetoplumbite blocks.

The first point, then, was to check the structure of crystals resulting from Na substitution for Ln in the β-aluminogallate structure and to see if the β structure is retained in such crystals obtained by ionic exchange:

—The characteristic diffraction spots of $P6_3/mmc$ are present with changes in intensities according to the amount of Nd^{3+} introduced in the lattice (*6*, *7*).

—The c/a ratio (close to 4) in the exchanged compound is consistent with loosely packed mirror-planes (hexagonal packing), as they occur in β-alumina-like lattice.

—The spectroscopic behavior of Nd^{3+} is quite different from that observed in the magnetoplumbite lattice (where its coordination number is 12) and rather similar to that of Nd^{3+} in β″ aluminas (coordination number lower than 9 (*5*, *14*)).

However, even after annealing treatments at ~700°C, the diffusion of neodymium in the inner part of the crystal is not achieved (*6*). Furthermore, as 3 Na^+ are replaced by 1 Ln^{3+} ion + 2 vacancies, some local ordering between Na, Ln, and vacant sites may occur on their sublattice; we are not concerned with local order here and, in this part, we only report an average structural description of a Nd^{3+} partly substituted compound. This will be the basis for further interpretation of short and long range ordering detected by X ray diffuse scattering in this compound. Actually, this local order strongly depends on the thermal history of the sample (ionic exchange temperature, annealing temperature etc.).

Besides the strictly structural interest, the average structure of such a Nd-exchanged β-alumina was sought for several reasons:

—To explain or confirm the optical behavior of Nd^{3+} in this β-alumina host-lattice and to compare it to the case of a MP matrix.

—To find whether Nd^{3+} is spread or not on several crystallographic sites, which would be of importance in the potential laser application.

—To see the variations in the crystal field around the lanthanide ion, owing to the presence of gallium (see introduction).

Experimental

The crystals were obtained, as described in Ref. (*6*), by immersion of Na β-aluminogallate, with a composition close to the preceding study (Al/Ga = $\frac{7}{4}$) in a melting $NdCl_3$–NaCl mixture, at 650°C. A small corner-edge of a Nd-exchanged crystal was selected for X-ray structural study, to ensure a Nd diffusion as homogeneous as possible (size: 0.2 × 0.3 × 0.05 mm) Intensities were collected on a four-circle diffractometer with operating conditions described in Table I.

Empirical absorption corrections were performed by the ψ scan. The distribution of Al/Ga on the sites of the spinel blocks was checked and confirmed to be similar to that of the starting Na crystal. Several tentative refinement cycles led to the localization of cations in the mirror-planes; atomic parameters for Nd are stable and well defined: neodymium is found quite close to the fixed 2d positions, whereas Na seems more disordered, distributed among two sites, with very high thermal factors (see Tables VI and VII).

Description of the Average Structure

This partly exchanged compound seems to retain the β-alumina type of structure. The high thermal vibrations for Na ions, shared between two sites, suggests a high disorder due either to an inhomogeneous structure or to the mobility of Na^+ ions, as previously observed in Na^+ fast ionic conductors. Main bond lengths are given in Table VII. Residual electron density is about 0.8e/Å^3 lying near the aBR site (0, 0, $\frac{1}{4}$).

The coordinates of the O3 ion should be noticed, as this atom is shifted out of its expected 2c Wyckoff position but toward the "BR" site occupied by Na^+ or Nd^{3+}. The presence of extra charges due to Nd^{3+} could explain this electrostatic attraction effect (Fig. 4).

Rather bad agreement is observed between experimental and computed 001 intensities; this can be due to disorder along the *c* axis. Successive mirror-planes may have different content or organization, with variable Nd/Na ratio or variable occupancy

TABLE VI

FINAL SET OF ATOMIC COORDINATES IN Na–Nd β-ALUMINOGALLATE (R = 0.049)

Type of atom	Wyckoff position	Coordination polyhedra	Coordinates			Thermal factor (isotropic B)
			x	y	z	
*M*1 Al	2a	Octahedron	0	0	0	0.33
*M*3 Ga	4f	Tetrahedron	0.3334	0.6667	0.0246(1)	0.23
*M*4 0.3Ga + 0.7Al	4f	Tetrahedron	0.3334	0.6667	0.1774(1)	0.39
*M*5 0.17Ga + 0.83Al	12k	Octahedron	−0.1675(2)	−0.3349	0.1083(1)	0.46
O1	4e		0	0	0.1433(3)	0.40
O2	4f		0.6667	0.3334	0.0573(3)	0.29
O4	12k		0.1530(5)	0.3061	0.0506(2)	0.22
O3	6h		0.3790(30)	0.7590	0.250	3.2
O5	12k		0.5043(6)	0.0086	0.1477(2)	0.45
Nd	6h (0.26) per plane		0.6892(6)	0.3784	0.250	2.5
Na1 (aBR)	2b (0.20) per plane		0	0	0.250	5.8
Na2 or O (mO)	6h (0.84) per plane		0.8009(34)	0.6018	0.240(43)	14.0

Note. Resulting total composition: $Nd_{0.26}Na_{0.77}Al_{7.4}Ga_{3.6}O_{17.27}$, determined as follows: 0.26 Nd^{3+} represent 0.78 positive charges. From the total of (0.84 + 0.20)Na^+, 0.22 Na added to Nd will balance the oxygen in the mirror-plane (β-alumina stoichiometric composition). The remaining "Na" corresponds to an excess of (x Na + x/2 O): 0.84 + 0.20 − 0.22 = 0.82 (Na + O), of which $\frac{2}{3}$ is Na(0.55) and $\frac{1}{3}$ is O(0.27). 1.03 site cationic site occupied (0.26Nd + 0.77 Na); 1.55 positive charge in mirror plane: [(0.26 × 3) + 0.77]; 0.27 excess oxygen in mirror plane.

TABLE VII

MAIN INTERATOMIC DISTANCES IN Nd-EXCHANGED ALUMINOGALLATE

Atomic site	Coordination number	Type of atom	M–O bond-lengths in Å	
M1(2a)	6	0.1 Ga + 0.9 Al	6 × O4	1.887(3)
M3(4f)	4	Ga	3 × O4	1.858(3)
			1 × O2	1.852(9)
M4(4f)	4	0.33 Ga + 0.67 Al	1 × O5	1.700(5)
			3 × O3	1.803(4)
M5(12k)	6	0.17 Ga + 0.83 Al	1 × O1	1.824(4)
			2 × O5	1.832(4)
			2 × O2	1.991(5)
			1 × O4	2.041(4)
Na1(6h)	8		2 × O3	2.44(3)
			4 × O5	2.74(1)
			2 × O1	3.09(1)
Na2(2b)	8		2 × O1	2.40(1)
			3 × O3	3.12(1)
			3 × O3	3.06(2)
Nd(2d)	9		4 × O5	2.75(1)
			2 × O5	2.94(1)
			2 × O3	2.71(1)
			1 × O3	3.04(1)

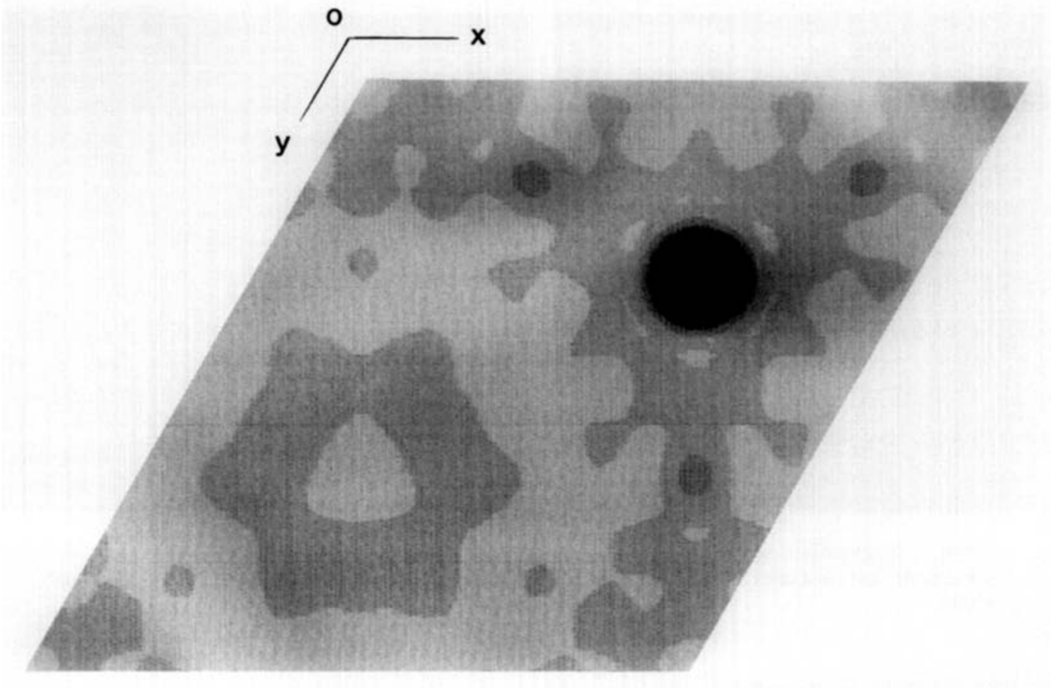

FIG. 4. Electron density map in the mirror-plane ($z = 0.25$) of Nd-exchanged Na^+ aluminogallate.

in the 2b (aBR) site: Na or vacancy may take this place in the lattice, with a disordered occurrence along *c*. Then, refinement cannot provide a satisfactory answer for a nonperiodic arrangement.

The composition of the studied crystal is drawn from the refined occupancy factors (described in Table VI): $Nd_{0.26}Na_{0.77}(Al_{7.3}Ga_{3.7})O_{17.27}$; 1.03 site cationic site occupied in the mirror-plane; 1.55 positive charge in the mirror-plane [(0.26 × 3) + 0.77]; 0.27 excess oxygen in the mirror-plane.

Heating treatments were performed to improve the homogeneity of our samples and to check their stability. They revealed that the structure is progressively modified upon heating; however, the crystal lattice is not destroyed and diffraction pictures are still of good quality:

—between 800 and 1000°C, a 2D local order is detected by X-ray diffuse scattering in the mirror-planes of the structure (Fig. 5),

—then, above 1200°C, ordering occurs in the third dimension, along the *c* axis,

—finally, over 1400°C, the crystals are decomposed.

The short-range order detected by X ray diffuse scattering could then be taken as the premise of a reorganization: first, Na/Nd/vac. ordering occurs in the mirror planes where ionic exchange takes place (and this might be easier for certain exchange rates), then order appears along the *c* axis, between mirrors having different types of arrangement, still to be determined.

As reported above (*14*), a mixed Na/Nd aluminate has been prepared at high temperature, by direct solid state reaction and melting. Under these conditions of elaboration, its structure is made of alternate β-alumina- and magnetoplumbite blocks (loosely packed mirror-planes with Na and

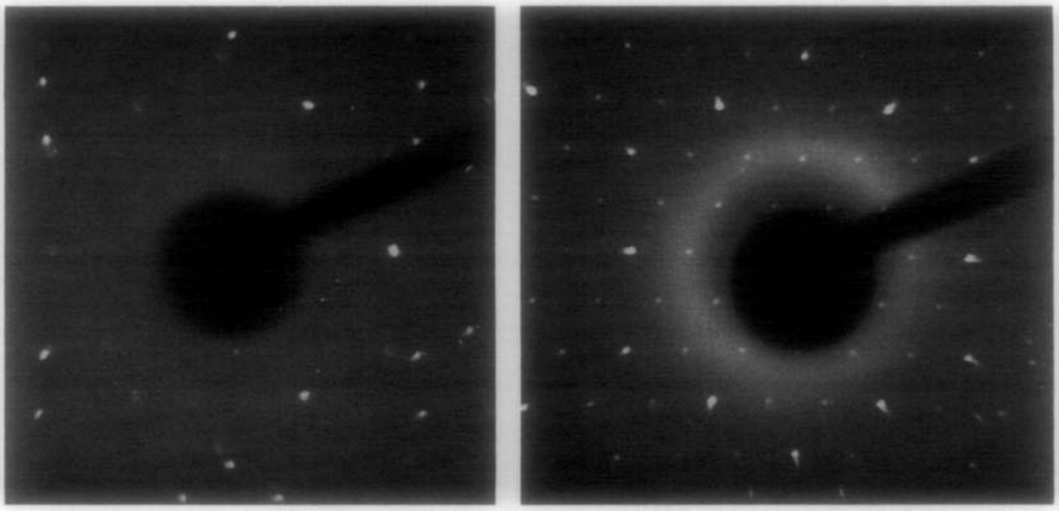

FIG. 5. X ray diffuse scattering in (00.1) planes of Nd-exchanged aluminogallate. Same orientation, same scale: left, just after Nd exchange (at 650°C); right, after heating in the temperature range 800–1200°C.

one O, or close-packed layers with Ln, Al, and 3O).

When ionic exchanges are performed on compounds with an initial structure of β-alumina type, the β-structure is first retained, as shown in the present paper. Then, one may assume that heating at higher temperatures could result either in a mixed structure or in a magnetoplumbite structure, according to the Nd content.

Conclusion

In both compounds having similar Al/Ga ratios, gallium is located mainly in fourfold coordination. In particular, Ga is found in tetrahedral sites close to the mirror planes of the structure, where Na ions lie. This probably favors the Na^+ mobility in these planes by further separating the neighboring oxygen layers and makes possible the partial ionic exchange by Nd^{3+}, which was not possible in pure Na β-aluminate.

As far as Nd-exchanged aluminogallate is concerned, this structural investigation brings the following conclusions:

—Exchanged crystals are of rather poor quality but clearly retain the β-alumina structure at the exchange temperature (650°).

—Nd^{3+} is located in a single position, slightly shifted from the theoretical one ($x = 0.687$ instead of 0.667), whereas Na^+ is highly disordered and scattered on two sites. Short-range order occurs in the loose-packed planes of the structure when the crystals are annealed at higher temperature.[1]

Acknowledgments

The authors are very grateful to M. Daran, from the Laboratoire de Chimie des métaux de transition, Université Pierre et Marie Curie, Paris, for performing careful data collection.

References

1. Y. F. YAO AND J. T. KUMMER, *J. Inorg. Nucl. Chem.* **29**, 2453 (1967).

---

[1] Supplementary material has been deposited with the editorial office.

2. J. P. Boilot, M. Lee, and Ph. Colomban, *J. Phys. Chem. Solids* **47,** 693 (1983).
3. B. Dunn and G. C. Farrington, *Mater. Res. Bull.* **15,** 1773 (1980).
4. B. Dunn and G. C. Farrington, *Solid State Ionics* **9–10,** 223 (1983).
5. M. Jansen, A. Alfrey, O. M. Stafsudd, B. Dunn, D. L. Yang, and G. C. Farrington, *Optics Lett.* **9,** 119 (1984).
6. G. Aka, J Théry, and D. Vivien, *Solid State Ionics,* **39,** 225 (1990).
7. G. Aka, Nouvelle thèse de doctorat es sciences-Université Pierre et Marie Curie, Paris 1988.
8. M. Bettman and C. R. Peters, Acta Crystallogr. **B27,** 1827 (1971).
9. W. L. Roth *J. Solid State Chem.* **4,** 60 (1972).
10. International Tables for X Ray Cristallography, IV, (1974), Kynoch Press, Birmingham, England.
11. A. Kahn, J. Lecomte, J. Théry, and D. Vivien, *J. Solid State Chem.* **76,** 192 (1988).
12. M. Gaspérin, M. C. Saine, A. Kahn, A. M. Lejus, and D. Vivien, *J. Solid State Chem.* **54,** 61 (1984).
13. D. Lefebvre, A. Kahn, and J. Théry, *C.R. Acad. Sci.* **300**(II), 263 (1985).
14. A. Kahn and J. Thery, *J. Solid State Chem.* **64,** 102 (1986).
15. G. Aka, J. Théry, and D. Vivien, *J. Electrochem. Soc.* in press.