Structural and Defect Study of Naβ''-Gallate by X-Ray Powder Diffraction Analysis

V. Massarotti, D. Capsoni, A. Marini, V. Berbenni, G. Flor, and C. Margheritis
Dipartimento di Chimica Fisica dell'Unversità di Pavia and C.S.T.E. C.N.R., Pavia, Italy

Z. Naturforsch. **46a**, 321–328 (1991); received January 7, 1991

The Rietveld profile refinement has been applied to X-ray powder diffraction data on Naβ''-gallate, a solid electrolyte isostructural with Naβ''-alumina and characterized by different types of lattice defect. Several structural models have been refined and discussed in order to understand if a statistical comparison of the structure discrepancy factors can be used as a reliable criterion to retain or reject structural changes from one model to the other. It is shown that, due to the correlation between structural parameters and to the poor sensitivity of the structure discrepancy factors to chemical composition, some care is necessary to direct correctly the refinement and to obtain a reliable structural model.

Key words: Powder diffraction, Profile refinement, Naβ''-gallate, Point defects, Solid electrolyte.

Introduction

Reliable structural investigations are usually performed on single crystal samples. When, however, materials of technological relevance are concerned, the main interest is generally on the study of the structure-properties relationship rather than on the structural study itself. Both physico-chemical properties and structural data should be obtained, in these cases, from samples as similar as possible to those in technological use. Since most ceramic materials are used in the form of sintered powders, the ability to obtain reliable structural data from powdered samples may be of great help. Rietveld analysis by both neutron and X-ray powder diffraction data [1, 2] has been recently used to refine quite complex structures containing various lattice defects such as substitutional defects [3–5], vacancies and intercalations [6].

The aim of this work, based on X-ray powder diffraction data, is to apply Rietveld analysis to Naβ''-gallate, a ceramic solid electrolyte isostructural with Naβ''-alumina. The Naβ''-alumina structure (S.G. R-3m) has been studied both by X-ray single crystal diffraction [7, 8] and by neutron powder diffraction data [9]. It can be schematically described as constituted by: a) *spinel blocks*, which consist of aluminum and oxygen planes characterized by a spinel-like stacking sequence, and represent the high packing part of the structure; b) *conduction planes*, which contain oxygen atoms and sodium ions and constitute the low packing part of the structure. The oxygen atom (O_5) occupies a well defined position and is tetrahedrically coordinated to the aluminum atoms of the spinel blocks. Sodium ions, on the contrary, show high mobility and are distributed over two not completely occupied lattice sites [7, 8].

The hexagonal elementary cell contains three spinel blocks spaced by three conduction planes at $z = 1/6$, $1/2$, $5/6$. The sodium content of the conduction planes is about 1.66 atoms/plane with the consequence that each conduction plane has an excess positive charge of about 0.66 electronic charges, corresponding to 2 excess positive charges per unit cell. Charge compensation is obtained by substitutional defects. Magnesium [7, 8] or lithium [9] atoms can substitute the aluminum atoms in the spinel blocks, leading to structure stabilization. No foreign atom is required, on the contrary, to obtain structure stabilization in Naβ''-gallate and charge compensation is obtained by substitution of immobile sodium atoms for gallium atoms of the spinel blocks [10].

The application of Rietveld analysis to Naβ''-gallate can be a useful test for the evaluation of the reliability of the method in assessing the presence of lattice defects (substitutional defects, interstitials and vacancies) in complex compounds with defect concentrations of about 0.5 defects per unit cell.

Reprint requests to Prof. V. Massarotti, Dipartimento di Chimica Fisica dell'Università di Pavia, viale Taramelli 16, 27100 Pavia, Italy.

0932-0784 / 91 / 0400-0321 \$ 01.30/0. – Please order a reprint rather than making your own copy

Experimental

Naβ''-gallate was prepared by solid state synthesis from Na_2CO_3 (Fluka 99%) and Ga_2O_3 (Fluka 99.99%). The mixture (molar ratio 1 Na_2CO_3 : 5.7 Ga_2O_3) was preheated one day at 900 °C in an open system in order to allow complete decomposition of sodium carbonate and then kept seven days at 1250 °C in a sealed platinum crucible. X-ray analysis of the powders so obtained showed the reflections of the β''-phase only.

As verified by TGA and X-ray measurements, water from air moisture can enter the conduction planes of Naβ''-gallate [11]. To avoid water intake, X-ray samples were kept in a dry atmosphere. Moreover, use was made of a polythermal attachment by which diffraction patterns were taken at room temperature after the samples were heated up to 400 °C and then cooled under vacuum.

Diffraction data were obtained in the step scan mode ($16^\circ < 2\Theta < 86^\circ$; step $= 0.02^\circ$; counting time: 20 s/step) by a Philips PW 1710 powder diffractometer equipped with a Philips PW 1050 vertical goniometer. The CuKα radiation was employed ($K\alpha_1 = 1.5406$; $K\alpha_2 = 1.5443$) along with a graphite bent crystal monochromator.

In the Rietveld profile procedure, together with the structural parameters, the following additional parameters were also refined: a) the background, by a four terms polynomial function; b) a preferred orientation parameter (P_1) by the function $P_K = \exp(P_1\ \alpha_K^2)$, where α_K is the acute angle between the scattering vector and the vector perpendicular to the crystallites; c) a scale factor; d) the zero error; e) the peak width (u, v, w) and shape (η); f) the peak asymmetry; g) the lattice parameters.

The refinements were continued till the parameter shifts became less than 30% of their associated e.s.d. The function minimized in the least squares procedure, and the computations of the weight factor of each observation, of the standard deviations, of the discrepancy factors R_p, R_{wp}, R_e and of the goodness of fit (R_{wp}/R_e), were exactly the same described in the program DBW 3.2 [12, 13]. The X-ray scattering factors for Ga^{3+}, Na^+ and O^- were selected from the incorporated list of f-coefficients. The calculation of the R_B factor has been modified according to Sakthivel [14].

Different profile functions were tested before selecting the pseudo Voigt one. The results are summarized in Table 1. Peak intensities were calculated over an angular range of twelve full widths at half maximum

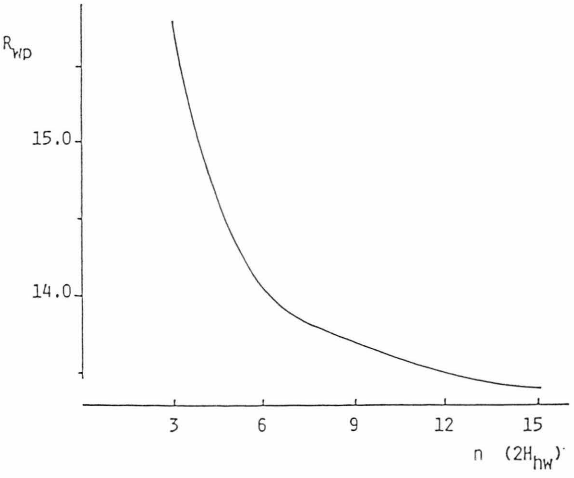

Fig. 1. Dependence of the discrepancy factor R_{wp} on the number of FWHM's over which the profile function is calculated. Profile function: Pseudo Voigt.

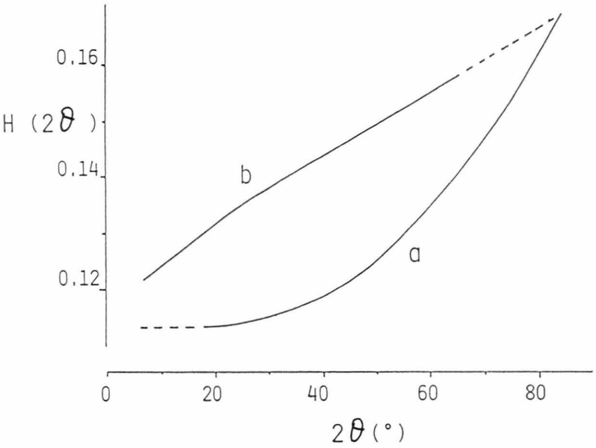

Fig. 2. Full width at half maximum (H) vs. diffraction angle. $H^2 = u\ \mathrm{tg}^2\ \Theta + v\ \mathrm{tg}\ \Theta + w$ (u, v, w: fit parameters). a) angular range 16°–86°; b) angular range 6°–66°.

Table 1. Discrepancy factors and asymmetry parameters obtained by using different profile functions on the same set of data.

Function	Conver. (cycle)	R_p	R_{wp}	Asymmetry parameters
P. Voigt	3	10.21	13.51	0.168(25)
Lorentzian	4	11.59	14.89	0.157(24)
Mod. 2 Lor.	4	11.17	15.03	0.650(78)
Mod. 1 Lor.	3	12.38	16.82	1.26 (16)
Gaussian	8	16.20	22.01	3.18 (98)
Pearson	div. (7)	–	–	–

(FWHM) on both sides of the peak centre. It can be seen that appreciably lower discrepancy factors are obtained with the pseudo Voigt function. It is, however, very important to select correctly the angular range (number of FWHM's) over which the profile function has to be calculated. The dependence of R_{wp} on this parameter is reported in Figure 1. The value of twelve FWHM's has been selected as an acceptable compromise by which the appreciable Lorentzian contribution, expecially to peak tails, can be taken into account without affecting too much the calculation time.

One more factor that was seen to considerably affect the fit quality is the angular range scanned during data acquisition. Figure 2 reports some of the results obtained by two refinements performed by using exactly the same variables on data acquired over two different angular ranges: $16° < 2\Theta < 86°$ and $6° < 2\Theta < 66°$. The full width at half maximum (H) has been obtained by the function:

$$H^2 = u \,\mathrm{tg}^2\,\Theta + v \,\mathrm{tg}\,\Theta + \mathrm{w} \quad [15].$$

It can be seen that the H vs. 2Θ behaviour is very different in the two cases. Moreover the fitting of the first data set shows a more rapid convergence and a noticeably lower discrepancy factor than the second one. The reason is that the fit of the first data set does not compare the calculated and experimental intensities of the 003 and 006 reflections which are greatly affected by asymmetry and preferred orientation. All the refinements have then been performed on data acquired in the angular range $16° < 2\Theta < 86°$.

Anisotropic thermal parameters (β_{ij}) have been used for Na_1, Na_2, and O_5 atoms, while isotropic (B) thermal parameters have been refined for all other atoms.

Table 2. Initial values of the positional (x, y, z), occupational (N) and thermal (B: isotropic; β: anisotropic) parameters utilized for the refinement of model A.

Atom	x	y	z	N	B
Ga_1	0.16656	−0.16656	−0.07302	18.000	0.975
Ga_2	0.00000	0.00000	0.35005	4.886	0.019
Ga_3	0.00000	0.00000	0.44973	5.670	0.310
Ga_4	0.00000	0.00000	0.00000	2.919	0.342
O_1	0.16118	−0.16118	0.03639	18.000	0.076
O_2	0.15868	−0.15868	0.23719	18.000	1.628
O_3	0.00000	0.00000	0.28984	6.000	0.183
O_4	0.00000	0.00000	0.09428	6.000	0.741
O_5	0.00000	0.00000	0.50000	3.000	*
Na_1	0.00000	0.00000	−0.16660	0.790	*
Na_2	0.2548	−0.2548	−0.16430	4.349	*
Na_3	0.00000	0.00000	0.35005	1.114	0.019
Ga_5	0.00000	0.00000	0.40230	0.411	1.250

* Atom	β_{11}	β_{22}	β_{33}	β_{12}
O_5	0.0139	0.0139	0.0031	0.0070
Na_1	−0.0672	−0.0672	0.0065	−0.0336
Na_2	0.0870	0.0870	−0.0009	0.0435

Results and Discussion

The positional and occupational parameters relevant to Naβ''-alumina [9] have been used as initial values for the refinement of the Naβ''-gallate structure. On this basis the starting model contains only one type of lattice defect: substitution of a sodium atom (Na_3) for a gallium atom (Ga_2) of the spinel block. Several refinements have been performed on this model and they all agreed in indicating that the main differences of Naβ''-gallate in respect to Naβ''-alumina are: 1) two gallium sites (Ga_3 and Ga_4) appear underoccupied; 2) the coordinates of some of the atoms of the unit cell are somewhat different; 3) the distribution of the sodium ions over the two different sites of the conduction plane is different.

To compensate for gallium deficiency, an additional interstitial site has been added (Ga_5), with the same $x = y$ coordinate as for Ga_3 and Ga_4 sites. As the gallium lack is much greater on the Ga_3 site than on the Ga_4 one, the initial z value of the interstitial gallium has been determined by seeking the interstice, nearest to the Ga_3 site, large enough to contain without large distortion an octahedrically coordinated gallium atom. A refinement has then been performed of the model (in the following referred to as model A) containing both the substitutional and interstitial defects. Occupational, positional and thermal parameters obtained by previous refinements have been used as initial values for all the atoms different from Ga_5. They are listed, together with those obtained for the Ga_5 interstitial, in Table 2. Model A contains 27 variable parameters. Variable positional parameters are constituted by the z values of Na_1, Na_2 and Ga_5 sites. Variable occupational parameters regard Na_1, Na_2, Ga_2, Ga_3, Ga_4 and Ga_5. Their changes are constrained in the following way: a) the occupation of the Ga_5 interstitial must equal the total gallium lack on $Ga_3 + Ga_4$ sites; b) the total occupation of the Ga_2 site (by $Na_3 + Ga_2$ atoms) must equal 6 atoms/cell; c) the total number of sodium atoms ($Na_1 + Na_2$) on the conduction plane must equal 5.14 atoms/cell.

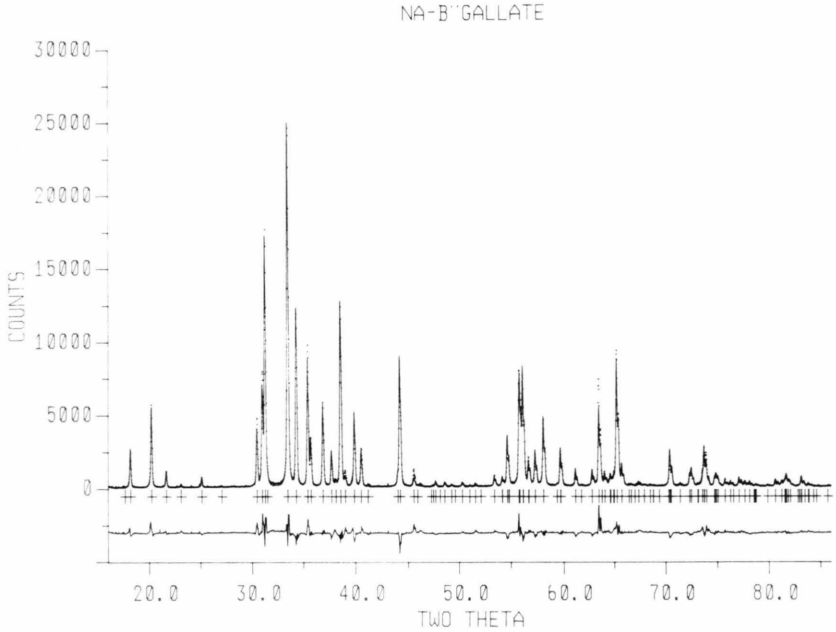

Fig. 3. Observed (·····) and calculated (——) patterns for Naβ''-gallate. The difference pattern is reported on the bottom. Marker signs indicate the position of the Bragg reflections for CuKα_1.

Table 3. Final values of the variable positional (x, y, z), occupational (N) and thermal (B; β) parameters obtained by model A. The refined lattice parameter values of the hexagonal cell are: $a = 5.85415(11)$; $c = 34.56456(70)$.

Atom	x	y	z	N	B
Ga_1	fixed	fixed	fixed	18.000	0.975
Ga_2	fixed	fixed	fixed	4.925(40)	0.019
Ga_3	fixed	fixed	fixed	5.680(18)	0.310
Ga_4	fixed	fixed	fixed	2.921(4)	0.342
O_1	fixed	fixed	fixed	18.000	0.116(165)
O_2	fixed	fixed	fixed	18.000	1.501(190)
O_3	fixed	fixed	fixed	6.000	0.091(320)
O_4	fixed	fixed	fixed	6.000	0.499(300)
O_5	fixed	fixed	fixed	3.000	*
Na_1	0.00000	0.00000	−0.1707(29)	0.788(90)	*
Na_2	0.2548	−0.2548	−0.1650(4)	4.352(90)	*
Na_3	fixed	fixed	fixed	1.075(40)	0.017
Ga_5	0.00000	0.00000	0.4013(11)	0.399(22)	1.250

* Atom	β_{11}	β_{22}	β_{33}	β_{12}
O_5	0.0213(107)	0.0213(107)	0.0030(5)	0.0107(54)
Na_1	fixed	fixed	fixed	fixed
Na_2	fixed	fixed	fixed	fixed

The refinement converges at the 5th cycle with $R_p = 10.05$, $R_{wp} = 13.36$ ($R_e = 3.55$), $R_B = 8.67$, which represent the lowest discrepancy factor values obtained in the course of the entire work. The experimental and calculated patterns of Naβ''-gallate are reported in Figure 3. The final values of the variable positional, occupational and thermal parameters are reported in Table 3.

Table 4. Naβ''-gallate bonding distances (in Å) as deduced by model A. Bonding distances of Mg [8] and Li [9] stabilized β''-aluminas are reported for comparison.

Coordination	Mean value	[8]	[9]
Tetrahedrons			
Ga_2–O_1: 3 × 1.8733			
O_3: 2.0811	1.925(104)	1.845(7)	1.824
Ga_3–O_2: 3 × 1.9043			
O_5: 1.7376	1.863(83)	1.742(41)	1.730(38)
Octahedrons			
Ga_1–O_1: 2 × 2.0895			
O_2: 2 × 1.8348			
O_3: 1.9752			
O_4: 1.8418	1.944(125)	1.909(71)	1.915(80)
Ga_4–O_1: 6 × 2.0623	2.062	1.891	1.891
Ga_5–O_1: 3 × 2.0540			
O_2: 3 × 2.0253	2.040(16)	–	–
Mobile cations			
Na_1–O_2: 3 × 2.9227		2.647	
O_4: 2.4997		2.502	
O_5: 3.3799		3.244	
Na_2–O_2: 2 × 2.7371		2.523	
3.3844		3.003	
O_4: 2.7036		2.578	
O_5: 3.0616		3.005	

The distribution of the sodium ions on the conduction plane is substantially unaffected by the introduction of the interstitial gallium atom and the occupation of the Na_1 site (0.79 atoms/cell) remains sensibly

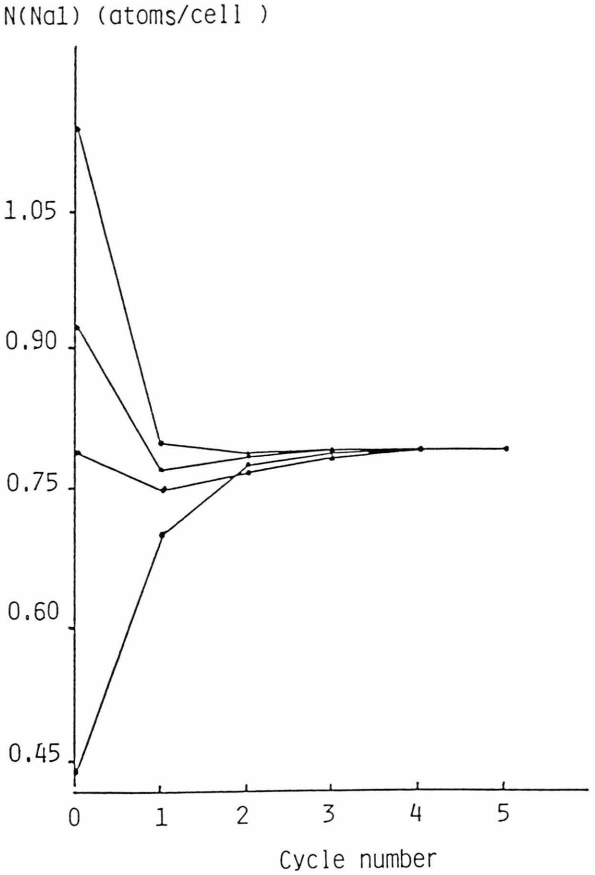

Fig. 4. Occupation of the Na_1 site vs. refinement cycle number. Constraint: $N(Na_1)+N(Na_2)=5.14$ atoms/cell.

lower than found by Roth et al. [9] for Naβ''-alumina (1.32 atoms/cell). To confirm the reliability of our value and to see if the final occupancy of the Na_1 site is somewhat affected by the initial occupation of the site, several refinements have been performed with different starting values. The results are shown in Figure 4. It can be seen that the final occupancy of the Na_1 site is totally independent on its initial value.

The interatomic distances pertinent to model A are reported in Table 4 together with the interatomic distances for magnesium [8] and lithium [9] stabilized β''-aluminas. If it is taken into account that a Ga–O bond is longer than a corresponding Al–O bond, it can be seen that there is a good correspondence between Ga–O and Al–O distances. It is to be noted that, owing to the presence of the substitutional defect and in agreement with Naβ''-alumina, the mean bonding distance Ga_2–O is longer than the Ga_3–O one.

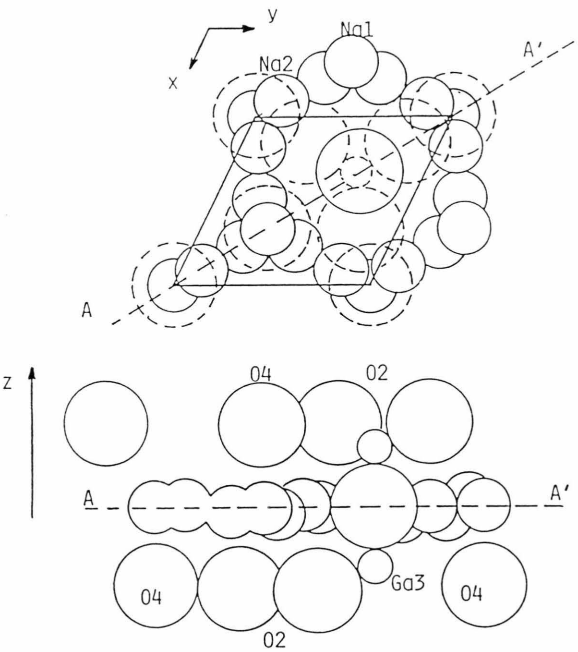

Fig. 5. Different views of Naβ''-gallate conduction plane.

Two different views of a conduction plane are reported in Fig. 5. Sodium ions form a continuum of positive charge sandwiched between oxygen planes. This accounts for the high mobility shown by sodium ions in Naβ''-gallate.

To assure that model A is a reliable one and to analyze the influence that structural and constraint variations might have on the results of the refinement, it is thought useful to discuss some of the refinements by which model A was obtained.

Model B does not contain interstitial gallium. Like in A the occupations of the Na_3+Ga_2 sites are constrained but, different from A, no constraint is kept on the occupations of the Ga_3+Ga_4 and Na_1+Na_2 sites. The main features of model B are summarized, together with those of all the other models discussed, in Table 5. As it can be seen, the discrepancy factors are all higher than those pertinent to model A, despite they have been obtained with one more variable parameter. From a statistical point of view model B must then be considered less probable than A. A comparison of the occupational parameters obtained by this model with those of model A shows that:

a) both Ga_3 and Ga_4 sites remain underoccupied. However, while the final occupation of the Ga_4 site remains substantially unchanged, that of the Ga_3 site increases from 5.68 to 5.80 atoms/cell;

Table 5. Summary of the main features of the structural models A, B, C, D, E, F. Y and N mean respectively presence or absence of the substitutional (S. Def.) and interstitial (I. Def.) defects. Together with the initial (I) and final (F) occupancy values of the different sites are also reported: the total number of variable parameters; the discrepancy factors R_p, R_{wp}, R_B ($R_e = 3.55$ for each model); the convergence cycle; the chemical formulae of the refined models.

Model	A	B	C	D	E	F
S. Def.	Y	Y	Y	N	N	N
I. Def.	Y	N	N	N	N	N
Ga_2 I.	4.88	5.28	5.28	6.00	6.00	6.00
Ga_2 F.	4.93(4)	4.80(5)	2.70(73)	5.23(3)	5.30(3)	6.00
Ga_3 I.	5.67	5.67	5.67	5.67	5.67	5.67
Ga_3 F.	5.68(2)	5.80(3)	5.80(3)	5.80(3)	5.73(4)	5.67
Ga_4 I.	2.92	2.92	2.92	2.92	2.92	2.92
Ga_4 F.	2.92(4)	2.91(2)	2.93(2)	2.91(2)	2.95(2)	2.92
Na_1 I.	0.79	0.79	0.79	0.79	0.79	0.79
Na_1 F.	0.79(9)	0.92(9)	0.90(9)	0.93(9)	0.81(9)	0.75(10)
Na_2 I.	4.35	4.35	4.35	4.35	4.35	4.35
Na_2 F.	4.35(9)	5.62(15)	5.52(15)	5.63(15)	4.33(9)	4.39(10)
Na_3 I.	1.12	0.72	0.72	–	–	–
Na_3 F.	1.07(4)	1.20(5)	7.1(2.0)	–	–	–
Ga_5 I.	0.40	–	–	–	–	–
Ga_5 F.	0.40(2)	–	–	–	–	–
Param.	27	28	29	28	27	24
R_p	10.05	10.48	10.51	10.48	10.67	11.29
R_{wp}	13.36	13.62	13.60	13.63	13.81	15.14
R_B	8.66	8.94	9.03	8.92	9.41	9.77
Conver.	5	5	6	5	5	10(NO)

	Chemical Formula
Model A	$3\,(Ga_{10.646(27)}Na_{0.359(13)}O_{16})\ (Na_{1.714}O)$
Model B	$3\,(Ga_{10.502(34)}Na_{0.401(16)}O_{16})\ (Na_{2.180(80)}O)$
Model C	$3\,(Ga_{9.809(262)}Na_{2.353(678)}O_{16})\ (Na_{2.140(82)}O)$
Model D	$3\,(Ga_{10.646(28)}O_{16})\ (Na_{2.187(80)}O)$
Model E	$3\,(Ga_{10.660(29)}O_{16})\ (Na_{1.714(62)}O)$
Model F	$3\,(Ga_{10.864}O_{16})\ (Na_{1.714(65)}O)$

b) the immobile sodium content (Na_3) of the Ga_2 site increases from 1.07 to 1.20 atoms/cell and, owing to the constraint to the total site occupation, the gallium content correspondingly decreases;

c) the occupation of both Na_1 and Na_2 sites increases (the latter much more than the former), leading to a total content of mobile sodium atoms of 6.54 atoms/cell.

The total occupation of $Ga_3 + Ga_4$ sites increases by 0.11 atoms/cell with respect to A. If, however, it is taken into account that the final occupation of the interstitial gallium site was 0.40 atoms/cell, it is easily seen that model B has a considerably lower electron density around Ga_3 and Ga_4 sites than A. A slight electron density decrease is also obtained for the Ga_2 site (considering the increased relative occupation of the site by Na_3) although the initial electron density on this site was higher than in model A. The only counter-balance to the electron density decrease of the spinel block is the sodium content increase on the conduction plane: when not hindered by constraints, the low density, disordered conduction plane can compensate for electron density changes taking place quite far from it.

The importance of constraints in defining the right way of the refinement can be even better seen by model C. This is totally identical to B except for the fact that the constraint to the occupation of the Ga_2 site (by $Ga_2 + Na_3$ atoms) has been eliminated. It can be seen that the occupation of Ga_3, Ga_4, Na_1 and Na_2 sites does not show any appreciable change with respect to B. Changes are on the contrary evident on the occupation of the Ga_2 site by Ga_2 and Na_3 atoms: the former considerably decreases while the latter greatly increases, with the result that their final values are no more compatible with the substitutional defect Na_{Ga2}. It is interesting to note that the electrons deficiency brought about by the gallium decrease, $(4.80 - 2.70) \times 28 = 58.8$, is nearly exactly counterbalanced by the electrons increase due to the increased sodium occupation, $(7.06 - 1.20) \times 10 = 58.6$. As a consequence, from the point of view of the electrons number, no appreciable difference exists between models B and C for what concerns the Ga_2 site. However, when a free selection is allowed to the system on how to reach the necessary electrons number on the site, a high sodium occupation is preferred. Moreover, on the statistical basis of the Hamilton test [16], no unambiguous selection is possible between the two models. This is a good example of the fact that adequate constraints can be necessary to correctly direct the refinement. In fact, if one takes into account that, for symmetry reasons, no more than 6 atoms/cell can occupy the Ga_2 site, the conclusion can be drawn that C represents an impossible model.

Problems can also arise from the poor sensitivity of the discrepancy factors to chemical differences. Model D does not contain substitutional sodium on the Ga_2 site. As can be seen in Table 5, models D and B have the same number of variable parameters and identical (R_p) or nearly identical (R_{wp} and R_B) discrepancy factors. No unambiguous selection is possible between these models on a purely statistical basis.

This confirms not only that discrepancy factors are quite insensitive to chemical differences, but it shows that such a poor sensitivity has the effect of making the selection of the right way for the refinement quite difficult: the substitutional sodium defect was introduced by analogy with Naβ''-alumina but no clear indication has been obtained by the refinement itself on the need of its presence.

It was noted, dealing with model C, that constraints were necessary to address correctly the refinement. This however is not always the case. Model E is identical to D except for the fact that the occupation of Na_1+Na_2 sites is constrained to a fixed value (5.14 atoms/cell). The comparison between models E and D by the Hamilton test shows that the increase of the discrepancy factors of model E over D is too high to be justified by the decrease of only one variable parameter and that, as a consequence, model D is more probable than E at the confidence level $\alpha=0.005$. However we know, on the basis of model A, that model D represents a worse structural approximation than E: both are different from A for what concerns the substitutional and interstitial defects of the spinel block but, while E has a similar situation on the conduction plane, D differs from A in this respect too. The statistical analysis of the discrepancy factors leads, in this case, to the selection of the "wrong" model. The reason is that, as previously noted, electronic deficiencies concerning the spinel block can be accommodated by the sodium ions of the conduction plane. When however the total occupation of the sodium ions is fixed as in E, this is no longer possible and the structure discrepancy factors indicate a less satisfactory structure refinement.

To confirm that the relationship between constraints and goodness of fit is a quite complex one, in model F constraints to the occupation of the gallium sites have been added to that of the sodium ions on the conduction plane: the Ga_2 site has been constrained to be occupied by 6 atoms/cell while the Ga_3 and Ga_4 sites have been constrained to maintain their initial occupation values. Table 5 shows that the refinement does not converge at the 10th cycle and the R_{wp} value, constant from the 7th cycle, is $R_{wp}=15.14$. Constraints are such that the electronic clouds of different sites can not compensate each other and no real increase of the goodness of fit is, as a consequence, possible.

Conclusions

It was seen that several experimental parameters can deeply affect the goodness of fit, which must then be optimized, as a first step of the refinement, by an appropriate selection of the same. When this is made, however, the problem arises of correctly selecting the number, type and initial value of the variable parameters by which a reliable structural model can be obtained. This is an important problem, and in general it must be solved by looking for the influence that a small change in a structural detail exerts on the structure discrepancy factors.

Some care is necessary in the interpretation of the results, owing to the correlation between structural parameters and to the poor sensitivity of the discrepancy factors to chemical composition. As a consequence of the first factor, structural errors can compensate each other, leading to models that look better than they really are. The problem can be overcome by introducing the necessary constraints between variable parameters, which in turn can be made only if the relevant structural details are known with the precision required to take them as reference points of the refinement.

A direct consequence of the second factor is the difficulty to detect substitutional defects. No clear indication was obtained by the refinement itself on the presence of the substitutional sodium defect: as shown by models B, C and D, more important in refining the structural situation of the Ga_2 site is the electron density on the site rather than the relative amounts of gallium and sodium atoms by which it is obtained. An opposite conclusion has however to be drawn for what concerns the interstitial defect. Its presence was clearly detected by the profile refinement, showing that useful structural information can be obtained by this method also in a highly defective structure such as that of Naβ''-gallate.

Acknowledgement

This work has been supported by MURST 40% funds.

[1] H. M. Rietveld, Acta Cryst. **22,** 151 (1967).
[2] H. M. Rietveld, J. Appl. Cryst. **2,** 65 (1969).
[3] M. A. Subramanian, P. R. Rudolf, and A. Clearfeld, J. Solid State Chem. **60,** 172 (1985).
[4] P. R. Suitch, J. L. La Cout, A. Hewat, and R. A. Young, Acta Cryst. **B 41,** 173 (1985).
[5] A. G. Nord, J. Appl. Cryst. **17,** 55 (1984).
[6] A. Santoro, M. Marezio, R. S. Roth, and D. Minor, J. Solid State Chem. **35,** 167 (1980).
[7] M. Bettman and C. R. Peters, J. Phys. Chem. **73,** 1774 (1969).
[8] J. P. Boilot, G. Collin, Ph. Colomban, and R. Comes, Phys. Rev. **B 22,** 5912 (1980).
[9] R. L. Roth, J. D. Jorgensen, and F. J. Rotella, General Electric Technical Information Series, No. 81CRD178, Schenectady, New York 1981.
[10] M. P. Anderson, L. M. Foster, and S. J. LaPlaca, Solid State Ionics **5,** 211 (1981).
[11] G. Flor, V. Berbenni, G. Chiodelli, A. Marini, and V. Massarotti, in: High Tech. Ceramics (P. Vincenzini, ed.), Elsevier, Amsterdam 1987, pp. 1971–1980.
[12] D. B. Wiles and R. A. Young, J. Appl. Cryst. **14,** 149 (1981).
[13] R. A. Young and D. B. Wiles, J. Appl. Cryst. **15,** 430 (1982).
[14] A. Sakthivel, Notice 87.1 to Users of Rietveld Analysis Programs DBW 2.9 and 3.2, Georgia Institute of Technology, Atlanta, GA 30332, 1987.
[15] G. Caglioti, A. Paoletti, and F. P. Ricci, Nucl. Instrum. **3,** 223 (1958).
[16] W. C. Hamilton, Acta Cryst. **18,** 502 (1965).