

Superstructure determination of the perovskite $\beta\text{La}_{0.33}\text{NbO}_3$

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New interesting results in the crystal structure of the perovskite $\beta\text{La}_{0.33}\text{NbO}_3$ were revealed using selected area electron diffraction, powder X-ray diffraction techniques and Rietveld refinement method. Although the superstructure of $\beta\text{La}_{0.33}\text{NbO}_3$ could not be seen by conventional X-ray powder diffraction technique, the electron diffraction patterns revealed weak spots resulting in a superstructure array for the atoms of $\beta\text{La}_{0.33}\text{NbO}_3$. The crystal symmetry is compatible with an orthorhombic cell, space group *Cmmm*. From Rietveld refinement, the resulting lattice parameters are: $a = 7.82(1) \text{ \AA}$, $b = 7.83(9) \text{ \AA}$, $c = 7.90(9) \text{ \AA}$ and goodness of fit $R = 0.1107$, $R_{wp} = 0.15$. The superstructure is built from distorted octahedra NbO_6 along the [001] axis. Results suggest that this distortion may be produced by occupation of La atoms in (2a) and (4l) sites. © 2000 Kluwer Academic Publishers

1. Introduction

In the 1960s, compounds of the family $\beta\text{Ln}_{0.33}\text{NbO}_3$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) were extensively studied as a way to understand the role of f electrons in chemical bonding. Nowadays these systems are reviewed because their promising properties as host crystals for Li^+ ion intercalation [1, 2], and due to their interesting electric and optoelectronic properties [3–7]. One of the most interesting characteristics to be mentioned in the structure $\beta\text{Ln}_{0.33}\text{NbO}_3$ is the position of La ions which are located in high symmetry sites. This is an important fact when studying spectroscopic properties since most works on non-radiate energy transfer processes involve trivalent lanthanide ions located at low symmetry sites. If La ions were located in a high-symmetry site, in principle, it should be easier to study and understand spectroscopic characteristics, because the lower number of crystal-field components there [8]. In addition, this crystallographic information should help to understand not only the influence of defects on the stability of the crystal but the relationship between crystal structure and physical characteristics like dielectric properties.

Although the structure of $\beta\text{La}_{0.33}\text{NbO}_3$ has been many times discussed and reviewed, many questions still remain unanswered. The crystal structure of $\beta\text{La}_{0.33}\text{NbO}_3$ was first proposed by Roth [9]. The structure of some compounds of the family $\beta\text{Ln}_{0.33}\text{NbO}_3$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Pr}, \text{Nd}$) were reported by Iyer [10]

who determined by single crystal X-ray diffraction an orthorhombic cell with lattice parameters, for lanthanum: $a = 3.911 \text{ \AA}$, $b = 3.917 \text{ \AA}$ and $c = 7.908 \text{ \AA}$. Although Iyer mentioned the possible existence of a superstructure in this compound which was already seen by Masuno [11], his work supports the Roth's model.

Recently, Tabira *et al.* [2] reported the presence of a superstructure in the $\beta\text{La}_{0.33}\text{NbO}_3$ compound using single crystal and synchrotron radiation.

As far as we know, no complete crystallographic data of the superstructure have been published. In this work the $\beta\text{La}_{0.33}\text{NbO}_3$ compound is studied by analyzing a set of characteristic electron diffraction patterns, the new resulting lattice parameters were used in a Rietveld refinement program for comparing with the observed X-ray data. New crystallographic data for this compound are reported and a global discussion among the different structural proposed models is presented.

2. Experimental

The compound $\beta\text{La}_{0.33}\text{NbO}_3$ was synthesized by solid state reaction. La_2O_3 and Nb_2O_5 were used as starting materials (purity $\geq 99.99\%$, Aldrich). Appropriate amounts of these oxides, in total 5 g, were mixed with acetone in an agate mortar. The mixture was fired in a Pt crucible at $1200^\circ\text{--}1350^\circ\text{C}$ for 3 to 5 days until

the reaction was completed. Powder X-ray diffraction pattern was registered by means of a Siemens D-5000 diffractometer (Cu $K_{\alpha 1}$ radiation, $\lambda = 1.54056 \text{ \AA}$) with a secondary graphite monochromator. A 2θ step size 0.02° was used. The Rietveld refinement was carried out by using a DBWS-9006 software into the CERIUStm interface [12].

Electron diffraction data were obtained by Selected Area Diffraction (SAD) techniques using a JEOL 1200 EX Transmission Electron Microscope. TEM samples were elaborated by transferring powder material on prepared standard Cu grids.

3. Results

3.1. X-ray powder diffraction

The X-ray diffraction patterns did not exhibit texture but revealed a high degree of crystallinity. The measured density was 5.12 g/cm^3 whilst the calculated density was 5.01 g/cm^3 . X-ray diffraction results were refined using the Rietveld method. Initial atomic positions were obtained from Iyer work [10] and the remaining positions for the supercell were generated by translation into the space group $Cmmm$. The crystal and refinement data for $\beta\text{La}_{0.33}\text{NbO}_3$ are listed in Table I. The X-ray refined powder pattern for $\beta\text{La}_{0.33}\text{NbO}_3$ is shown in Fig. 1. A good fitting between the experimental and calculated data is observed. The R_w , R_{expected} and S values, were slightly higher compared to the standard values and DWD is slightly small. Additional efforts were carried out without success for diminishing the goodness of fit values.

The experimental data for the interplanar spacing, the relative intensities and the (hkl) indices for $\beta\text{La}_{0.33}\text{NbO}_3$ are shown in Table II. As it was previously mentioned, the intensities corresponding to superstructure distances could not be detected by X-ray diffraction even with very long time steps.

The refined atom positions and thermal parameters, obtained from the DBWS-9006 program, are listed in

TABLE I Crystal and refinement data for $\beta\text{La}_{0.33}\text{NbO}_3$

$\beta\text{La}_{0.33}\text{NbO}_3$	
Crystal system	Orthorhombic
Space group	$Cmmm$ (65)
Lattice parameters (\AA)	$a = 7.82(1)$ $b = 7.83(9)$ $c = 7.90(9)$ $\alpha = \beta = \gamma = 90^\circ$
Volume (\AA^3)	484.941
Z	8
Calculated density (g/cm^3)	5.01
Exp. Density (g/cm^3)	5.12
Refined pattern range 2θ	8–110
Step scan increment (2θ)	0.02
Wavelength (λ)	1.54056
No. of contributing reflections	368
R	0.11
R _w P	0.15
R_{expected}	7.18
S	2.19
DWD	0.41

TABLE II Powder diffraction data for $\beta\text{La}_{0.33}\text{NbO}_3$

hkl	$2\theta_{\text{obs}}$ ($^\circ$)	d_{obs} (\AA)	d_{calc} (\AA)	I/I°
001	11.217	7.8816	7.909	55
002	22.506	3.9478	3.955	47
200	22.761	3.9036	3.911	49
021	25.382	3.5061	3.512	18
220	32.353	2.7648	2.768	100
003	34.107	2.6265	2.636	4
221	34.333	2.6098	2.608	10
203	41.308	2.1838	2.186	2
040	46.330	1.9581	1.960	40
400	46.441	1.9536	1.955	40
223	47.632	1.9075	1.909	22
240	52.202	1.7508	1.752	8
421	53.641	1.7071	1.708	8
224	57.245	1.6097	1.609	36
422	57.522	1.5990	1.600	18
043	58.687	1.5718	1.573	1
025	63.392	1.4660	1.467	7
044	67.237	1.3913	1.392	20
404	67.325	1.3896	1.390	20
244	71.980	1.3116	1.311	2
424	72.044	1.3097	1.310	5
442	72.288	1.3059	1.306	4
026	76.157	1.2489	1.249	7
260	76.896	1.2387	1.239	8
620	77.062	1.2365	1.237	6
444	85.602	1.1336	1.134	19
263	86.785	1.1212	1.121	3

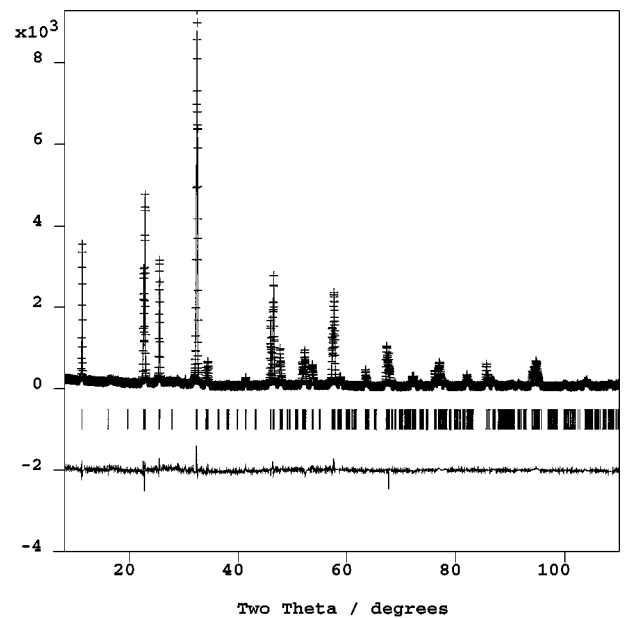


Figure 1 X-ray refined powder diffraction pattern of $\beta\text{La}_{0.33}\text{NbO}_3$.

Table III. In the proposed model, the La1 and the La2 positions are occupied at 44% with respect to their particular position occupation, the total number of La atoms in the structure is 2.666. The stoichiometry of the compound is $\beta\text{La}_{0.33}\text{NbO}_3$ with $z = 8$.

Recently, Tabira *et al.* [2] reported the presence of a superstructure in the $\beta\text{La}_{0.33}\text{NbO}_3$ compound using single crystal and synchrotron radiation.

From the International Tables of Crystallography the $Cmm2$, $Cm2m$, $Cmmm$, $C2mm$ and $C222$ groups belong to the same Laue class and have the same extinction symbol C—, they are indistinguishable for the used

TABLE III Fractional atomic coordinates and thermal parameters for $\beta\text{La}_{0.33}\text{NbO}_3$

	x/a	y/b	z/c	B (\AA^2)	Occ.	W
La(1)	0.00	0.00	0.00	1.55229	0.07001	2a
La(2)	0.00	0.50	0.00	1.55229	0.08176	4l
Nb	0.25	0.25	0.2631	1.55229	0.50	8m
O(1)	0.00	0.2706	0.2545	1.15009	0.50	8n
O(2)	0.2612	0.00	0.22011	1.64467	0.50	8o
O(3)	0.25	0.25	0.00	1.15009	0.25	4e
O(4)	0.25	0.25	0.50	1.15009	0.25	4f

techniques. However, among these groups the $Cmmm$ is the only one which allows the whole atoms being located in atomic particular positions.

3.1.1. Structure description

The $\beta\text{La}_{0.33}\text{NbO}_3$ compound has a perovskite related structure, where the lanthanum atoms occupy dodecahedral sites and the Nb^{5+} ions are located in octahedral sites. Original perovskite structure [10] reported in literature would have the 12 coordinated cavities form planes at $Z=0$ and $Z=1/2$. For our structure $Z=1/2$ sites are empty while $2/3$ of the $Z=0$ sites are randomly occupied by the rare earth atoms. Nb ions are displaced from the centers of the octahedra. The NbO_6 octahedra were found to be greatly distorted, thus making identification of the tilt system difficult.

An interesting feature of this cation-deficient perovskite structure is the numerous vacant sites at 0, 0, $1/2$, which are situated, on average 2.758 \AA , far from the nearest oxygen atom in the structure; it means that an atom could easily be accommodated in such place. This is a very important result that is related with conductivity phenomena. The structure, which was obtained using the Cerius²™ program [12] is shown in Fig. 2.

The ratio La1 La2 is 1 : 2. It is very important to keep this ratio constant in order to maintain the peaks of the supercell with their observed intensity. According to our simulations, if this position is not considered, the supercell peak (110) would appear more intense, Fig. 3. In Fig. 4, the geometry of the polyhedron of coordination of the NbO_6 octahedra is presented. In this figure it can be seen the distortion for distances and angles. Due to the poor occupation of the La atoms in both sites, this effect could be explained in terms of the statistical occupation of such places. The selected bond distances and angles are listed in Table IV.

3.2. Electron diffraction results

The indexed diffraction electron patterns which were obtained from powdered of $\beta\text{La}_{0.33}\text{NbO}_3$ showed additional spots which correspond to a supercell. The supercell was orthorhombic, with lattice parameters: $a = 7.82(2) \text{ \AA}$, $b = 7.83(8) \text{ \AA}$ and $c = 7.90(8) \text{ \AA}$. The relationship between the supercell lattice parameters and those of the simple lattice are then $a = 2af_1$, $b = 2bf_1$ and $c = cf_1$.

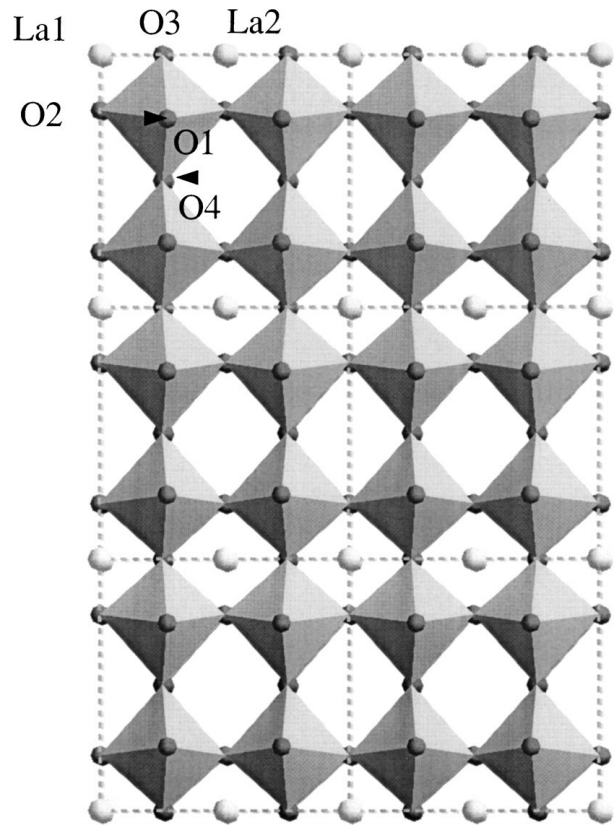


Figure 2 Scheme of the supercell for $\beta\text{La}_{0.33}\text{NbO}_3$ where the Nb cations are located in the octahedral centers.

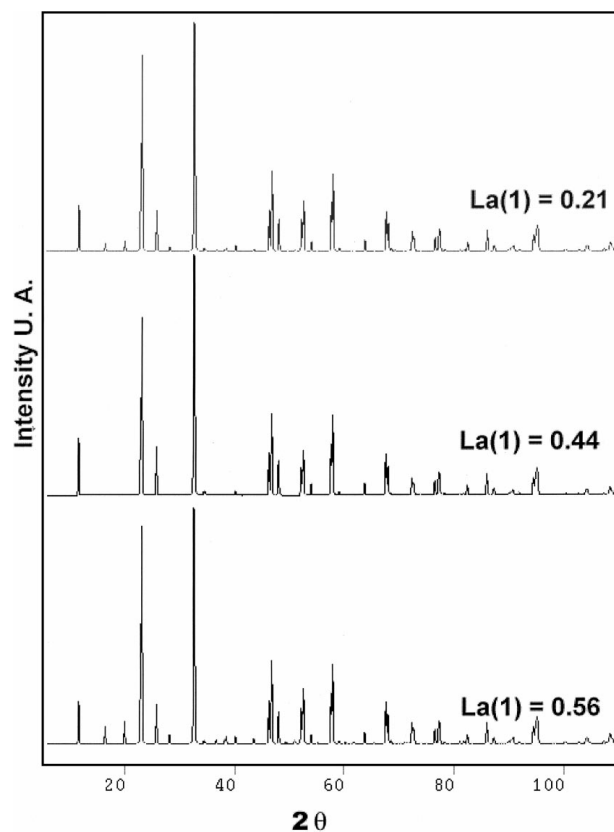


Figure 3 Calculated X-ray powder patterns as a function of La(1) occupation.

TABLE IV Selected bond lengths (Å) and angles (°)

$\beta\text{La}_{0.33}\text{NbO}_3$	(Å)
Nb–O1	1.963
Nb–O2	1.993
Nb–O3	2.081
Nb–O4	1.874
$\beta\text{La}_{0.33}\text{NbO}_3$ -1	(°)
O1–O4	92.0
O4–O2	99.8
O2–O1	96.8
O1–O3	88.0
O3–O2	80.2
O2–O1	96.8
$\beta\text{La}_{0.33}\text{NbO}_3$ -2	(°)
O1–O4	92.0
O4–O2	99.8
O2–O1	82.5
O1–O3	88.0
O3–O2	80.2
O2–O1	82.5

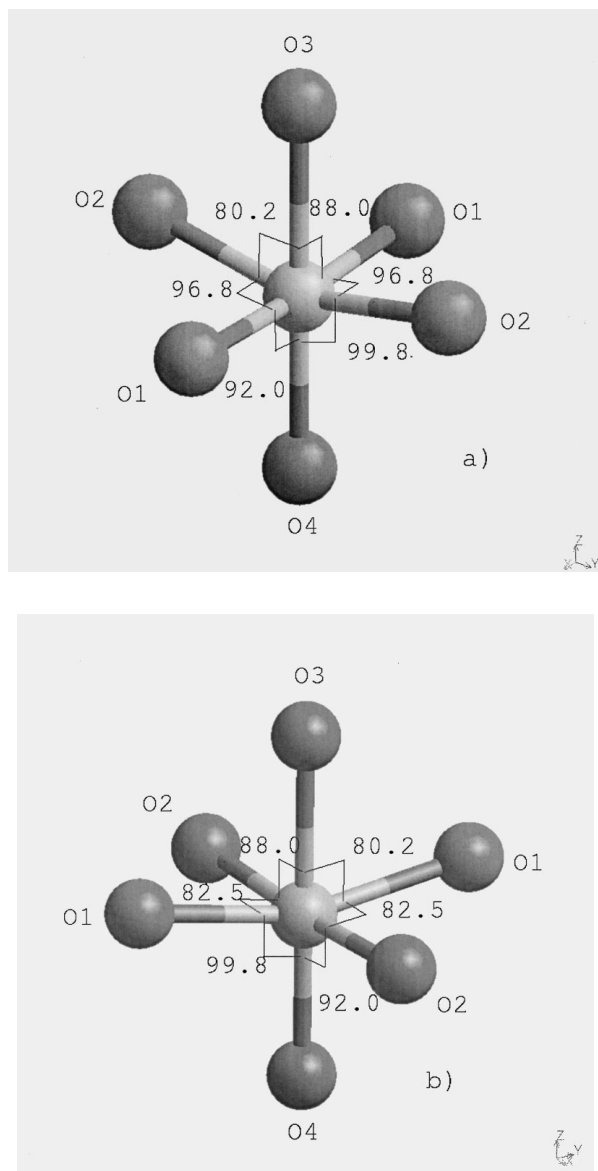


Figure 4 NbO₆ octahedra in the supercell showing the difference in the angles between them.

Five different zone axes, where the spots of the supercell are well defined were chosen. As it was expected, the intensities of the supercell structure were weaker than those of the simple cell. The extinctions presented in electron diffraction patterns, confirmed these absences, according to the general extinctions, $[(hkl): h + k = 2n]$, the following groups $Cm2m$ and $Cmmm$ apply as well. The electron diffraction patterns and their location within a stereographic projection are shown in Fig. 5.

4. Discussion and conclusion

In this work the existence of a supercell in the structure of the $\beta\text{La}_{0.33}\text{NbO}_3$ compound was observed by electron diffraction however, careful analysis of the X-ray diffraction patterns did not reveal any feature which could be related with the presence of a superlattice. One difficulty in the superstructure determination is that the intensity of superlattice reflections that directly results from the small displacements of the atoms is generally very weak.

Even when the supercell peaks were not seen by X-ray diffraction, it was possible to carry out a Rietveld refinement, in which the peaks of the supercell were assumed in the refinement to have very small intensities.

Starting from the simulations it could be noted that the peaks of the supercell were correlated with a particular occupation of the La atoms. The evolution of a characteristic interval where it is shown the correlation of the supercell peaks and the occupation of La atoms is shown in Fig. 3. It is important to point out that in order that the structure factor of the supercell peaks are as small as they appear it is necessary that the ratio of atoms of La atoms at their places (2a), (4l) are exactly 0.44. Any change in this proportion will make appear the peaks of supercell.

It was observed from Rietveld simulation:

When the La(1) and La(2) occupation factor were 1, there was a systematic extinction of the superstructure peaks (110).

Supercell peaks (110) always appears when the ratio of La(1) and La(2) occupation factor was different of 0.44. In upper values of the supercell peaks were not visible in the X-ray powder patterns. On the other hand the best results in Rietveld analysis were obtained when the occupation factor of La(1) = La(2) was 0.44.

This supercell is conceived like a statistical occupation of the La atoms into their positions (2a) and (4l). This result was supported by TEM, X-ray powder diffraction and Rietveld analysis of the proposed structure.

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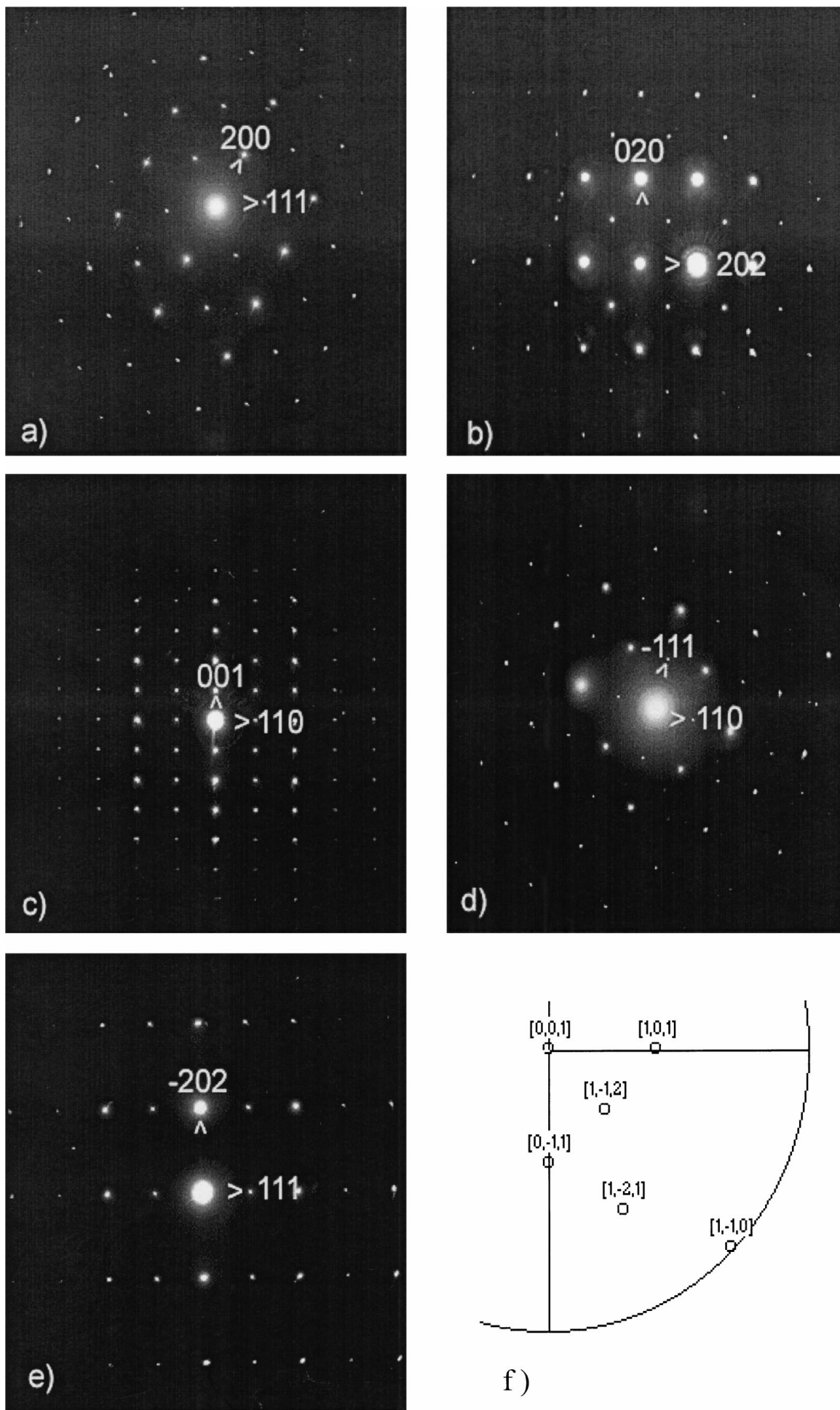


Figure 5 Main electron diffraction patterns of $\beta\text{La}_{0.33}\text{NbO}_3$ compound with zone axis: a) $[\bar{1}1]$, b) $[101]$, c) $[1\bar{1}0]$, d) $[1\bar{1}2]$, e) $[11\bar{2}]$ and f) stereographic projection.

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