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Review

Solving Structural Problems of Ceramic Materials*

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- *ab-initio* structure solution
- ceramics
- ternary system La_2O_3–Nb_2O_5–TiO_2
- defect perovskite

Methods for the crystal structure determination from powder diffraction data are reviewed with special emphasis on the application to technical ceramics. Experimental techniques using other than laboratory X-ray, such as synchrotron radiation, neutron and electron beams, are also described. As an illustrative example, the crystal structure determinations of compounds $LaNbTiO_6$, $La_{0.462}Nb_{0.614}Ti_{0.386}O_3$ and $La_{0.37}Nb_{0.889}Ti_{0.111}O_3$ in the ternary system of La_2O_3–Nb_2O_5–TiO_2 are reported.

INTRODUCTION

Recent time has witnessed a fast development of new technologies, which are closely connected with the development of new materials. Ceramics, traditional-classical (silicate ceramics comprising clay products, cements, glasses) and modern-technical (oxide and non-oxide ceramics), also belong to technologically very important materials. This is especially true of »electronic« ceramics due to their insulating, semi-conductive, dielectric, piezoelectric or magnetic properties. Knowledge of the reactivity of ceramics systems at high temperatures is necessary for the development of quality ceramics. The high temperature state in the system is described by a phase equilibrium diagram. The diagram itself and the knowledge of structures of phases appearing in it are the basis for further development of ceramics with desired characteristics. This paper presents the methods of determination of such structures and gives an illustrative example of structural characterization of one part of the phase equilibrium diagram of the ternary system of La_2O_3–Nb_2O_5–TiO_2.

METHODS OF STRUCTURE DETERMINATION OF COMPOUNDS BELONGING TO TECHNICAL CERAMICS

Compounds belonging to technical ceramics are typically synthesized by solid state reactions, which last for several hours or days at high temperatures, often exceeding 1000 °C, with intermittent cooling, grinding and remixing. The product is usually polycrystalline material. There are special methods[1] (Verneuil method, Czochralski method, zone melting, flux method) for single crystal preparation, but all require hard and long-lasting work and a very skillful experimenter. Even with all this, suitable single crystals are not always obtained. Provided single crystals are obtained, their X-ray or neutron dif-

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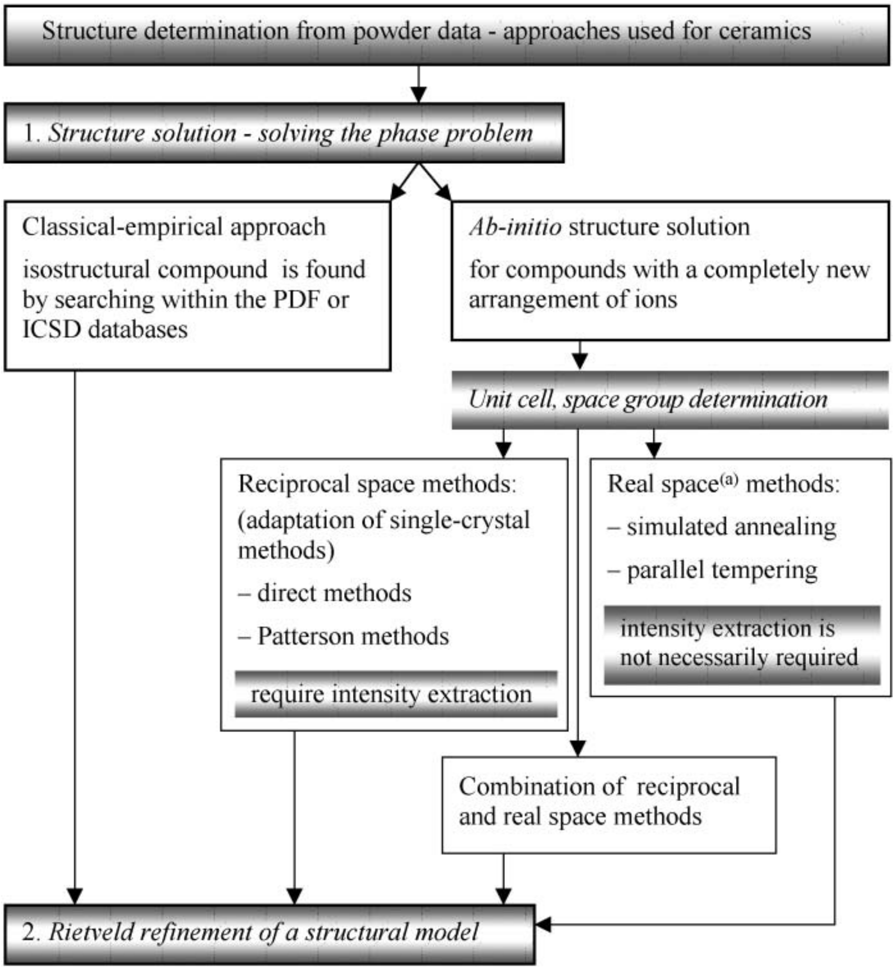
** Author to whom correspondence should be addressed. (E-mail: amalija.golobic@uni-lj.si) fraction pattern gives more accurate and precise results than the powder techniques due to the loss of information caused by the collapse of three-dimensional information available from the single crystal to the single dimension of a powder diffraction pattern. Unfortunately, the preparation of a powder sample of ceramic material suitable for structure determination is not easy either. The reaction conditions, temperature, pressure and especially the composition of the reaction mixture have to be carefully controlled to obtain the desired compound without impurities and of sufficient crystallinity.

Structure Determination from Powder Diffraction (SDPD)

If a suitable single-crystal is not available, then an alternative method of structure determination from powder diffraction (SDPD) has to be used. A schematic overview of different methods that have been used for structure determination of compounds belonging to ceramics is shown in Scheme 1. The SDPD methods have been developed and expanded dramatically during the last twenty years,[2] resulting in a large increase of the number of structure determinations in this way and of the number of independent atoms in these structures. The common feature of all approaches is the final Rietveld refinement[3] while the method of obtaining a structural model is specific to each method. There are many different SDPD approaches,[2] but only a few have been applied to ceramic materials.

The most widely used is the classical-empirical approach, where the model of isostructural compound can be found by searching through the Powder Diffraction File, PDF[4] (comparing the experimental powder pattern with those included in PDF, which now contains also calculated powder diffraction patterns of all structures included in the Inorganic Crystal Structure Database, ICSD[5]) or by direct examination of ICSD[5] (comparing unit cell parameters or looking through structures with the expected formula). This approach is often successful since many times new ceramic compounds consist of simple anions (O^{2-}, N^{3-}, C^{4-}…) and many different metal cations, which are arranged in a similar way as some other kind of ions in some already known structure. Using this approach, we have determined the structures for compounds $LaNbTiO_6$, $La_{0.462}Nb_{0.614}Ti_{0.386}O_3$ and $La_{0.37}Nb_{0.889}Ti_{0.111}O_3$; three ternary compounds in the system of La_2O_3–Nb_2O_5–TiO_2, which is described in a separate section at the end of this paper.



Scheme 1. Schematic ordering of the methods of structure determination from powder data, used for ceramic compounds. ([a]This approach has already been used for inorganic, metallic hydrides but not yet for oxides.)

When the ions of a new ceramic compound arrange in a completely new way, forming a new structure type, only *ab-initio* structure solution is possible. These methods can be divided into two groups: reciprocal space methods and real space methods.[6,7]

Reciprocal Space Methods. Thus far most of the *ab-initio* solutions for ceramic materials have been done using this method, where after indexing, space group determination and intensity extraction procedures, the phase problem is solved using or adapting single crystal structure solution methods (direct or Patterson methods). It has to be emphasized that none of the above mentioned steps is simple and errors and problems are encountered with each one, which has the consequence that these methods do not lead so straightforwardly to the final solution as in the case of a single crystal. Even with the correct unit cell parameters and space group, the structure solution many times fails due to the overlap of the reflections. The problem is that all methods of partitioning the peak intensities to the individual Bragg reflections (Pawley,[8] Le-Bail[9]) in the case of overlapping reflections leave some errors in the extracted intensities. Nevertheless, many structures of compounds belonging to ceramic materials have been determined in this way. Tables I and II provide a list of structures of oxide ceramics, determined by reciprocal space methods. Table I lists the structures where the phase problem was solved by direct methods using SIRPOW,[10] MULTAN,[11] SHELXS[12] and EXPO[13] programs, which revealed the positions of metal cations. Introduction of these atoms and refinement of their positions, followed by the difference Fourier synthesis led to the location of oxygen atoms. After getting positions of atoms of a partial model, this can be used to improve partitioning in a new intensity extraction procedure. The final structural model obtained using extracted intensities was finally refined by the Rietveld refinement using the whole powder diffraction pattern. In the case of structure determination of oxide compounds included in Table II, the process was very similar, differing only at the stage of locating the heavy atom, which was done by the Patterson method.

TABLE I. The list[62] of metal oxides whose structures were determined from powder data by the reciprocal space – direct methods

Formula	Year of publication	No. of atoms in the asymm. unit	Ref.
$Al_2Y_4O_9$	1987	6	63
$LaMo_5O_8$	1988	14	64
$LiSbWO_6$	1988	6	65
$LiBiPd_2O_4$	1989	4	66
NiV_2O_6	1990	15	67
Cr_8O_{21}	1991	15	68
$BaBiO_{2.5}$	1991	5	69
$Li_2PdP_2O_7$	1992	6	70
$Li_8Bi_2PdO_{10}$	1993	11	71
$La_3Ti_5Al_{15}O_{37}$	1994	60	72
$Li_{29}Zr_9Nb_3O_{40}$	1994	16	73
Bi_2CdO_4	1994	6	74
$Li_{0.43}Na_{0.36}CoO_{1.96}$	1994	9	75
$FeVMoO_7$	1995	10	76
$Fe_4V_2Mo_3O_{20}$	1995	16	77
$Sr_6Co_5O_{15}$	1995	8	78
$NaBi_2Sb_3O_{11}$	1995	6	79
$PbPt_2O_4$	1996	9	80
ε-WO_3	1997	8	81
$Fe_2V_4O_{13}$	1997	19	82
$BiCa_2VO_6$	1998	7	83
$AlVMoO_7$	1998	8	84
$K_2ZrGe_2O_7$	1999	7	85
$BaCaGa_4O_8$	1999	6	86
$La_2Mo_4O_{15}$	2001	21	87
$BaFeO_{2.8-\delta}$	2001	10	88
δ-$ZrMo_2O_8$	2001	5	89
$Bi^{III}{}_3Bi^{V}O_7$	2002	12	90
Bi_3SbO_7	2002	12	90

Real Space Methods comprise model building,[14] Monte Carlo method,[15] simulated annealing,[16,17] parallel tempering[18] and genetic algorithm.[19–20] The common feature of these methods is that they try to find a structural model in real space by random shifts of atoms or building blocks (molecules, polyhedra); these trial models are evaluated by a comparison of the corresponding calculated diffraction pattern with the observed one and they do not necessarily require extraction of the intensities of individual reflections, which is one of the critical steps in the reciprocal space methods. Intense work has

TABLE II. The list[62] of metal oxides whose structures were determined from powder data by the reciprocal space – Patterson methods

Formula	Year of publication	No. of atoms in the asymm. unit	Ref.
$K_2ZnGe_2O_6$	1989	7	91
β-Tl_3VO_4	1991	5	92
$CuPt_3O_6$	1991	10	93
$Tl_4V_2O_7$	1992	5	94
$Ca_{0.2}Na_{0.9}Fe_{2.905}$	1993	16	95
$Li_6Zr_2O_7$	1993	8	96
$CaTl_2O_4$	1995	5	97
$Ca_2Tl_2O_5$	1995	6	97
$Ca_3Tl_2O_6$	1995	12	98
$Ca_3Tl_4O_9$	1995	9	99
$Li_{0.98}Ti_{2.88}O_6$	1998	6	100

been done during the past ten years to develop these methods, but mostly for organic, molecular crystals. One reason that these methods were not used for compounds belonging to ceramics is that the chemical knowledge about the structural formula, connectivity of atoms in a compound is extremely helpful when using these methods, since incorporating this information into the starting model reduces the degrees of freedom and thus reduces the number of trials when compared to the situation of a completely random distribution of all atoms. In the case of molecular compounds the knowledge of the structural formula is a routine, which is not the case of inorganic compounds. Nevertheless, the situation is not so difficult, since solid state NMR, EXAFS and other spectroscopies can also give useful information about the coordination sphere of cations and also structural data of already known structures can be used to build polyhedra (*e.g.*, TiO_6 octahedron) in order to reduce the degrees of freedom. These possibilities have just recently been implemented in the new program FOX[6] and also in TOPAS.[21] FOX has already been successful in solving some inorganic structures – metal hydrides.[22–25] Thus, there are perspectives also for metal oxides.

On the other hand, an approach that combines reciprocal and real space methods was recently applied in the structure determination of $BiPb_2VO_6$[26] and LaW_2O_9[27]. In this approach, metal ions were located by the reciprocal space – direct methods and since difference Fourier mapping failed to reveal oxygen atoms positions, the latter were located by the application of simulated annealing (real space method).

As already mentioned, after finding the structural model, this has to be refined by the Rietveld refinement, where structural and profile parameters are fitted in order to achieve the best possible fit of the calculated powder diffraction pattern to the observed one. It has also to be emphasized that it is not enough to get excellent agreement between those two patterns if the final structure is not chemically reasonable, *e.g.,* if atoms are too close to each other or there are too large empty spaces.

Application of Synchrotron Light, Neutron and Electron Diffraction to Structural Studies of Ceramics

Many structural studies of ceramic materials are done using synchrotron X-ray, neutron or electron diffraction methods or a combination thereof.[28–32]

Synchrotron X-ray light is used because of the high resolution of diffraction data, which reduces the problem of the overlap of reflections. Another advantage of the synchrotron beam is that many different wavelengths of the primary beam are available and that one can be chosen to diminish absorption problems in the case of capillary measurements.

Neutron diffraction has an important role in the structure determination of ceramic compounds for many reasons. First, the X-ray scattering power of O^{2-}, N^{3-}, C^{4-} is much lower than that of most metal cations in ceramic compounds while this is not true of their scattering power towards neutrons. Consequently, neutron diffraction is essential for getting accurate positions and occupancies of these lighter atoms. Neutron diffraction studies[28,30,31] sometimes reveal slightly different positions of O atoms than those obtained by X-rays, resulting in a unit cell of lower symmetry (superstructures). Second, neutron diffraction is also used to distinguish between atoms that have similar X-ray scattering power such as Mn/Fe or Co/Ni, since their neutron scattering powers (cross sections) are different. Finally, since only neutrons detect the ordering of electron spins whereas X-rays do not, the neutron diffraction is also essential for magnetic structure analysis. Ferro, ferri and antiferromagnetic[33] properties of magnetic ceramic compounds are studied in this way.

Electron diffraction is also frequently used, not only because it is carried out by means of an electron microscope, which is part of the ceramic laboratory standard equipment, but also for its advances in unit cell and space group determination, especially when there are doubts or problems with indexing the X-ray powder pattern. Many superstructures were also revealed in this way.[29,31] In the past, due to significant problems with extinction, the intensities were useless for structure analysis. It has been shown recently[32,34,35] that electron crystallography (electron diffraction together with HREM images) can be applied successfully also for structure determination. Specimen preparation is an important and not simple step in electron diffraction techniques and ceramic samples are very suitable also from this point of view.

STRUCTURAL CHARACTERIZATION OF TERNARY COMPOUNDS FROM THE $LaNbTiO_6$–$La_{1/3}NbO_3$ TIE LINE IN THE SYSTEM La_2O_3–Nb_2O_5–TiO_2

Ceramics based on some compounds in the La_2O_3–TiO_2 system have interesting dielectric properties.[36–39] This is especially true of the unstable perovskite compound $La_{2/3}TiO_3$.[40] This compound can be stabilized by a small addition of other oxides like Al_2O_3[41,42] or Ga_2O_3[43]. The ceramics based on $La_{2/3}TiO_3$–$LaAlO_3$ solid solution exhibit very good dielectric properties in the microwave frequency range.[44] Since the perovskite compound $La_{1/3}NbO_3$ was reported to be stable in the La_2O_3–Nb_2O_5 system[45] we wondered if it could also stabilize $La_{2/3}TiO_3$. Thus, we decided to carry out a study on subsolid phase equilibria in the ternary system of La_2O_3–Nb_2O_5–TiO_2. As part of this work we report here the crystal structures of three compounds, $LaNbTiO_6$ (**1**), $La_{0.462}Nb_{0.614}Ti_{0.386}O_3$ (**2**) and

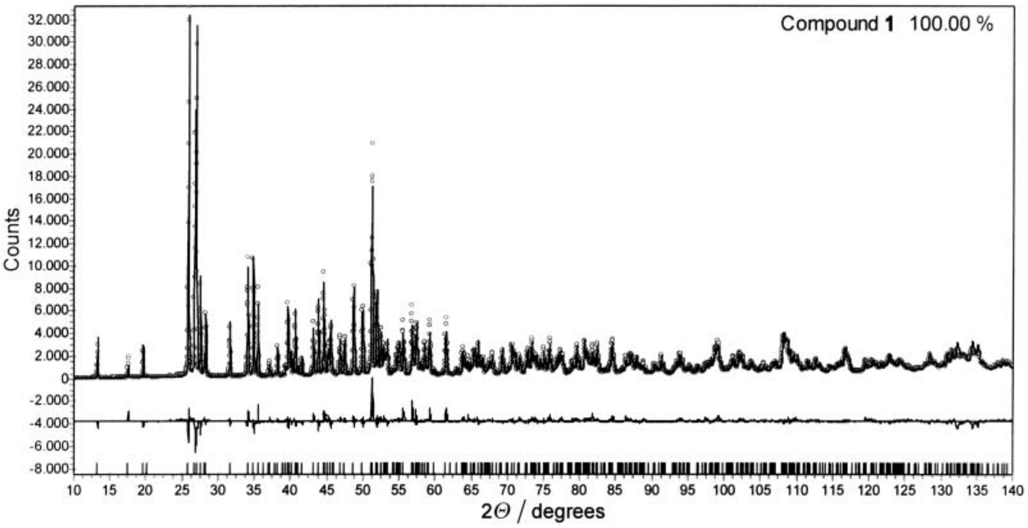


Figure 1. Experimental (circles), calculated (solid line) and difference (lower solid line) profiles of compound **1**. Vertical bars denote the positions of reflections.

$La_{0.37}Nb_{0.889}Ti_{0.111}O_3$ (**3**) from the $LaNbTiO_6$–$La_{1/3}NbO_3$ tie line in this ternary system. In the literature, four structures containing only La, Nb, Ti and O are reported: the orthorhombic form of $LaNbTiO_6$[46] and three perovskite-type structures $La_{0.63}Nb_{0.08}Ti_{0.92}O_3$[47], $La_{0.633}Nb_{0.10}Ti_{0.90}O_3$[48] and $La_{0.64}Nb_{0.08}Ti_{0.92}O_3$[49]. The powder diffraction file PDF contains, besides the calculated[46] and observed patterns[50,51] of orthorhombic $LaNbTiO_6$, also the observed indexed powder pattern of the monoclinic form[52] whose structure is reported in this paper.

Experimental Procedure

Compounds **1**, **2** and **3** were prepared by the solid state reaction technique at 1300 °C starting from oxides according to the scheme: $(2–x)/6\ La_2O_3 + (1–x)\ TiO_2 + x/2\ Nb_2O_5 \rightarrow La_{(2–x)/3}Nb_xTi_{(1–x)}O_3$, where x = 0.500, 0.614, and 0.889 for compounds **1**, **2** and **3**, respectively. EDAX and X-ray structural analysis confirmed the empirical formulas of all three compounds obtained by the synthesis. Details of the synthesis of compounds **1**, **2** and **3** and the results of the measurements of their microwave dielectric properties will be reported elsewhere.

TABLE III. Data collection parameters

Instrument	Bruker D-4
Radiation	Cu-Kα
Temperature	25 °C
Voltage, current	40 kV, 30 mA
Specimen	flat-plate
Soller slit	primary and secondary 2.3°
Variable slit	6 mm
Receiving slit	0.1 mm
Monochromator	secondary, graphite – only for **2** and **3**
Detector	Sol-X for **1**, scintillation counter for **2** and **3**
Range of 2*θ*	10–140°
Step width	0.026°
Time per step	60, 48, 48 s for **1**, **2**, **3** respectively

The X-ray diffraction patterns were collected on a Bruker D-4 diffractometer with a θ–2θ Bragg-Brentano geometry. Data collection was aimed at the highest possible resolution and sufficiently good statistics (especially at high angles) to enable a meaningful refinement. Details are given in Table III. To obtain stronger intensities also at higher angles, the data were collected using a variable divergence slit. The sample was exposed to the beam *via* a 6 mm long slit through the whole 2θ range.

The structures of all three compounds were solved using the classical-empirical approach. The powder diffraction pattern of compound **1** matched that of the monoclinic modification of $LaNbTiO_6$ with known unit cell parameters but with an unknown structure. Examination of ICSD revealed that $ThTi_2O_6$[53] has very similar unit cell parameters and the appropriate formula. Its structure, where Th^{4+} was replaced by La^{3+} and half of Ti^{4+} sites were randomly exchanged by Nb^{5+}, was successfully used for a structural model of compound **1**. The powder diffraction pattern of compound **2** is very similar to that of the orthorhombic modification of $LaNbTiO_6$.[46,50,51] Its structure is known[46] and was applied for the structure solution of **2** taking occupancy parameters 0.924, 0.614 and 0.386 instead of 1.0, 0.5 and 0.5 for La^{3+}, Nb^{5+} and Ti^{4+}, respectively. Compound **3** is a solid solution of $La_{2/3}TiO_3$ in $La_{1/3}NbO_3$. Consequently, its powder diffraction pattern is very similar to that for the right end member of the solid solution, *i.e.*, to $La_{1/3}NbO_3$. The latter has a defect perovskite structure, which was first described in 1967 by the single crystal film technique as a tetragonal structure in the *P*4/*mmm* space group.[45] Compared to the well known cubic perovskite structure of ABX_3,[54] Nb^{5+} are on B sites, while La^{3+} are with the occupancy 2/3 on every second A site along the *c* axis, leaving the remaining half of them vacant and causing a

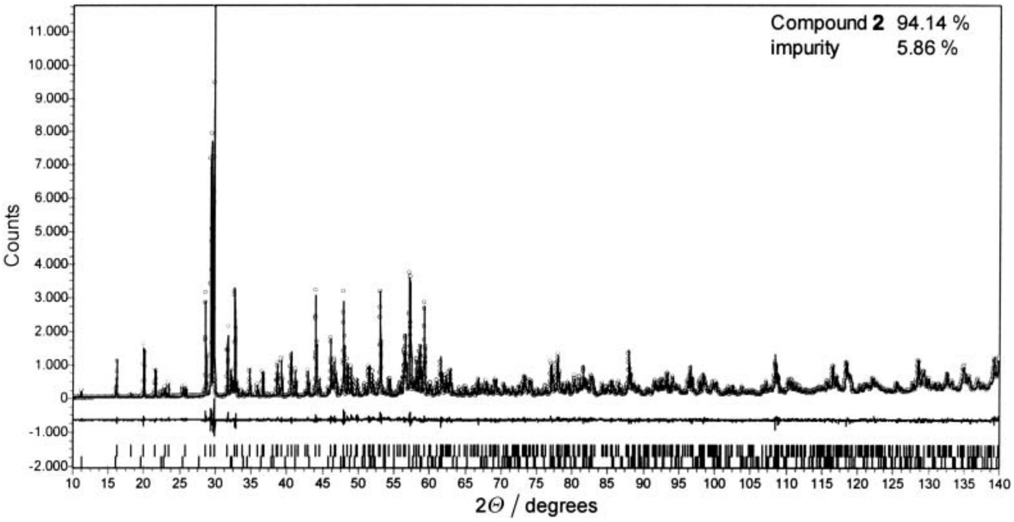


Figure 2. Experimental (circles), calculated (solid line) and difference (lower solid line) profiles of compound **2**. Upper vertical bars denote the positions of reflections of the main phase and the lower those of the impurity, compound $La_{0.377}Nb_{0.87}Ti_{0.13}O_3$.

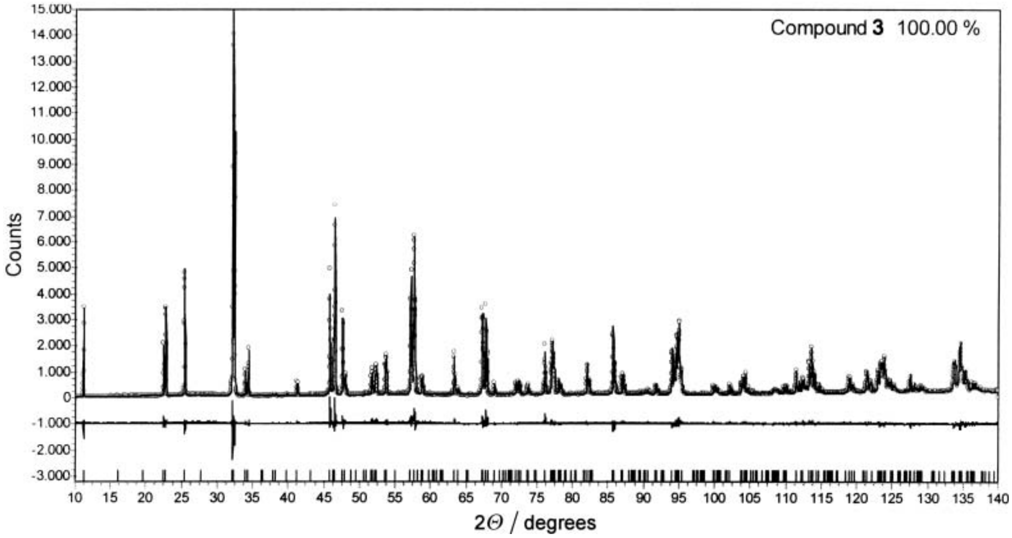


Figure 3. Experimental (circles), calculated (solid line) and difference (lower solid line) profiles of compound **3**. Vertical bars denote the positions of reflections.

doubling of the *c* cell edge. Later on, the structure was re-determined as orthorhombic in the *Pmmm* space group with small differences between *a* and *b* edges.[55] Only recently two independent studies, one by neutron[28] and the other by electron[29] diffraction, established its superstructure: due to small tilts of NbO_6 octahedra, the *a* and *b* edges are also doubled and the resulting space group is *Cmmm*. Since X-ray scattering power of O atoms is small compared to La, Ti or Nb, the superstructural peaks caused by small displacements of O atoms from special positions were very weak in the X-ray diffraction pattern and the superstructure was discovered by the electron and neutron diffraction. In the X-ray powder diffraction pattern of compound **3,** we have found the corresponding very weak reflections (Figure 4) that indicate such a superstructure, so the same supercell was taken for indexing the reflections and *Cmmm* for a space group. The structure of $La_{1/3}NbO_3$[28] was used for a structural model for solving the structure of **3,** where 11.1 % of Nb^{5+} sites were randomly replaced by Ti^{4+} and by taking the occupancy of La^{3+} 74.1 % instead of 66.7 %.

The TOPAS2.1 program[21] was used for the refinement and profile plotting. Intensities of the observed and calculated patterns matched well after the first few cycles, refining only the scale factor and three background parameters. In the refinement of the unit cell parameters, the diffractometer zero point and two profile parameters were gradually added. For calculation of the profile, the fundamental parameters approach (FPA)[56–59] was used, where there are two kinds of contributions to the profile: an instrumental and a phase dependent one. In our case, we kept the instrumental parameters fixed and refined only the crystallite size and one micro-strain parameter. After that, we refined the atomic coordinates and atomic isotropic displacement parameters as well. The latter were constrained to be equal for equal types of atoms. In our calculations, we set and kept the occupancy parameters according to the synthesis and EDAX analysis. Just for the purpose of checking, we also refined the population parameters and the results were close to the experimental values. Finally, we included one parameter into the refinement to correct the preferred orientation and

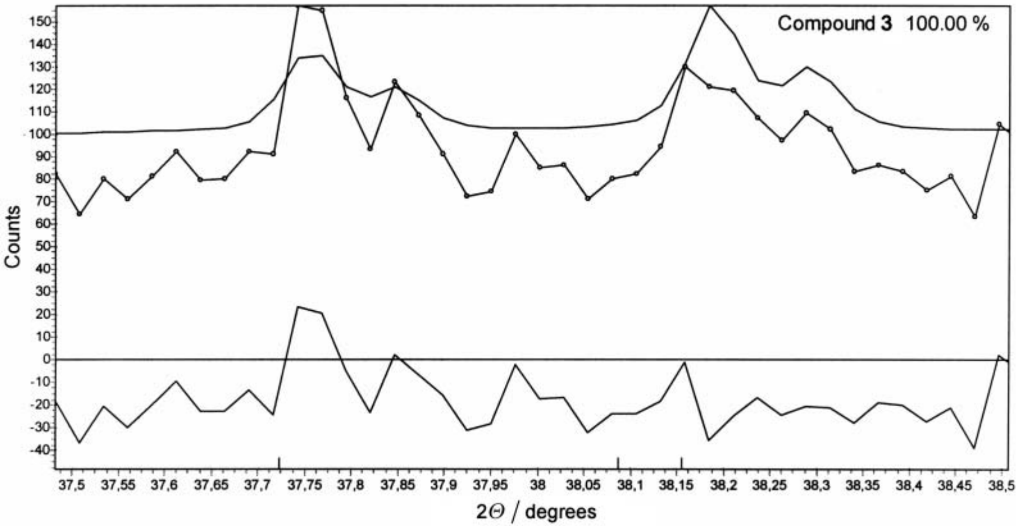


Figure 4. Enlarged region of the powder pattern of compound **3**, showing the appearance of weak superstructural reflections.

three additional parameters for description of the background. In the case of compound **2,** the sample contained impurity, $La_{0.377}Nb_{0.87}Ti_{0.13}O_3$, which is in the phase diagram linked with compound **2** by the tie-line and is the left end member of the solid solution of $La_{2/3}TiO_3$ in $La_{1/3}NbO_3$. To get more accurate structural parameters of the main phase and to achieve a better fit between the calculated and observed parameters, we included the structure of $La_{0.377}Nb_{0.87}Ti_{0.13}O_3$ into the refinement, where we refined its cell and one strain parameter and its fraction. The final calculated patterns in all three cases agreed well with the observed ones (Figures 1–3), which also means satisfactory *R* factors. The final refinement parameters for all samples are listed in Table IV, atomic parameters in Tables V–VII. The final structural data (including coordinates, displacement

TABLE IV. Crystal data and refinement parameters of compounds **1**, **2**, **3**

	1	2	3
Formula	$LaNbTiO_6$	$La_{0.462}Nb_{0.614}Ti_{0.386}O_3$	$La_{0.37}Nb_{0.889}Ti_{0.111}O_3$
Formula – asymm. unit	$La_{0.5}Nb_{0.5}Ti_{0.5}O_3$	$La_{0.462}Nb_{0.614}Ti_{0.386}O_3$	$La_{0.1852}Nb_{0.4444}Ti_{0.0556}O_{1.5}$
M_{rel} of asymm. unit	187.85	187.70	93.67
Crystal system	monoclinic	orthorhombic	orthorhombic
Space group	*C*2/*c*	*Pnma*	*Cmmm*
a / Å	11.2041(1)	10.96305(7)	7.80411(5)
b / Å	8.85114(9)	7.58996(5)	7.82272(5)
c / Å	5.27180(6)	5.46833(3)	7.92310(5)
β / deg	115.3282(7)	90.00	90.00
V / Å^3	472.545(9)	455.015(5)	483.700(5)
Z	8	8	16
powder color	pale yellow	pale yellow	pale yellow
D_x / Mg m^{-3}	5.283	5.482	5.147
No. of profile points	5000	5000	5000
No. of reflections	461	474 + 291 of impurity	292
No. of struct. param.	20	21 + 3 of impurity	14
No. of profile param.	11	11 + 2 of impurity	11
R_p	0.0682	0.0623	0.0766
R_{wp}	0.0887	0.0836	0.1069
R_{exp}	0.0280	0.0561	0.0542
R_{Bragg}	0.0497	0.0205	0.0357

$R_p = (\Sigma|y_i(\text{obs}) - y_i(\text{calc})|)/\Sigma y_i(\text{obs})$; $R_{wp} = \sqrt{((\Sigma w_i(y_i(\text{obs}) - y_i(\text{calc})))^2/\Sigma w_i(y_i(\text{obs}))^2)}$; $R_{exp} = \sqrt{((N - P)/\Sigma w_i y^2_{oi})}$;
$R_{Bragg} = (\Sigma|I_k(\text{obs}) - I_k(\text{calc})|)/\Sigma I_k(\text{obs})$; where y_i is intensity above background in step i, w_i is weight in step i, I_k is intensity of k^{th} Bragg reflection, N is no. of step intensities and P is no. of parameters.

TABLE V. Atomic fractional coordinates, occupancies and isotropic displacement parameters for compound **1**

	x	*y*	*z*	Occupancy	$B_{\rm iso}$
La	0.5	0.69440(11)	0.25	1.0	0.712(21)
Nb	0.26743(12)	0.91857(16)	–0.4487(3)	0.5	0.67(3)
Ti	0.26743(12)	0.91857(16)	–0.4487(3)	0.5	0.67(3)
O1	0.3615(5)	0.9177(7)	–0.0325(12)	1.0	0.18(7)
O2	0.6423(5)	0.7543(6)	0.0316(12)	1.0	0.18(7)
O3	0.6400(5)	0.5354(7)	0.6525(14)	1.0	0.18(7)

TABLE VI. Atomic fractional coordinates, occupancies and isotropic displacement parameters for compound **2**

	x	*y*	*z*	Occupancy	$B_{\rm iso}$
La	0.45841(8)	0.7500	0.04006(18)	0.924	0.137(17)
Nb	0.64392(9)	0.50523(14)	0.4632(2)	0.614	0.362(19)
Ti	0.64392(9)	0.50523(14)	0.4632(2)	0.386	0.362(19)
O1	0.4758(6)	0.4632(7)	0.2712(11)	1.0	0.13(7)
O2	0.2904(6)	0.9445(8)	–0.1328(12)	1.0	0.13(7)
O3	0.3558(7)	0.75	0.4569(17)	1.0	0.13(7)
O4	0.6246(8)	0.75	0.3519(15)	1.0	0.13(7)

TABLE VII. Atomic fractional coordinates, occupancies and isotropic displacement parameters for compound **3**

	x	*y*	*z*	Occupancy	$B_{\rm iso}$
La	0.5	0.7478(7)	0.0	0.741	0.221(19)
Nb	0.7514(7)	0.5	0.26293(11)	0.889	0.503(17)
Ti	0.7514(7)	0.5	0.26293(11)	0.111	0.503(17)
O1	0.7275(18)	0.5	0.0	1.0	0.48(7)
O2	0.7753(17)	0.5	0.5	1.0	0.48(7)
O3	0.5	0.5	0.244(3)	1.0	0.48(7)
O4	0.5	1.0	0.219(2)	1.0	0.48(7)
O5	0.75	0.75	0.2353(13)	1.0	0.48(7)

and geometrical parameters) have also been deposited with FIZ Karlsruhe Crystal Structure Deposition (CSD) Center as supplementary material under the deposition numbers from 413439 to 413441 for compounds **1** to **3**, respectively. Copies of the data can be obtained, free of charge, by contacting crysdata@fiz-karlsruhe.de.

Description of the Structures

Figures 5 and 6 represent the structure of compound **1** along *b* and *a** axes, respectively. The structure contains layers, parallel to the (100) plane, formed by distorted Nb/TiO$_6$ octahedra sharing three edges in a similar way as AlO$_6$ octahedra in aluminum hydroxide.[60] In-between these layers are layers of La^{3+} ions, with similar arrangement as in one plane of the La metal but, of course, with larger separations (from 4.335(1) to 5.272(1) Å). Each La atom is surrounded by eight O atoms at distances from 2.391(7) to 2.748(7) Å. The Nb/Ti–O distances range from 1.925(6) to 2.048(6) Å.

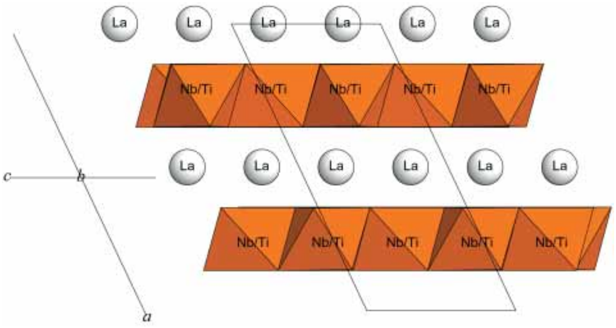


Figure 5. Projection of the structure of compound **1** along its *b* axis.

The structure of compound **2**, shown in Figure 7, is built up of pairs of distorted Nb/TiO$_6$ octahedra with

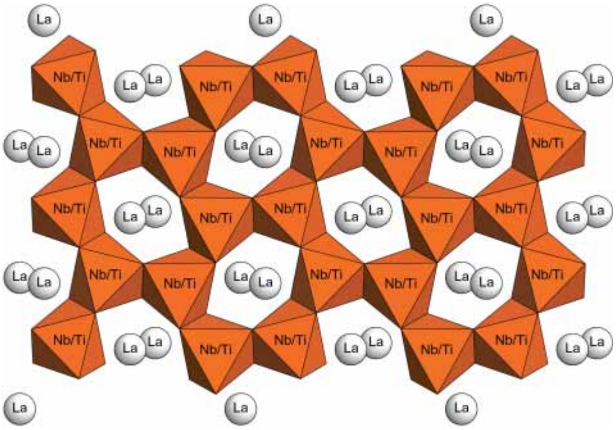


Figure 6. Projection of the structure of compound **1** along its *a** axis.

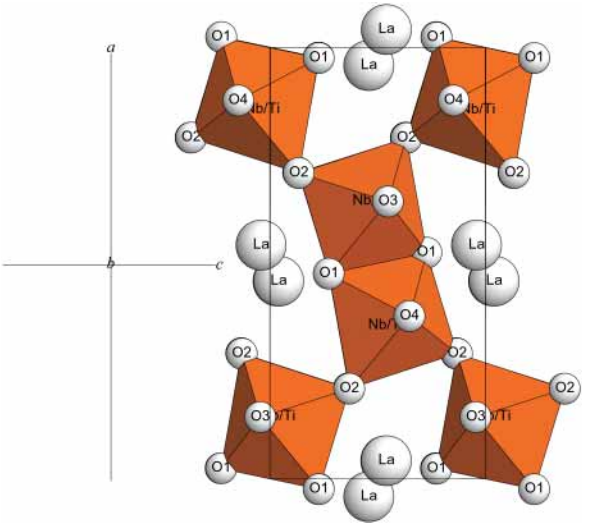


Figure 7. Projection of the structure of compound **2** along its *b* axis.

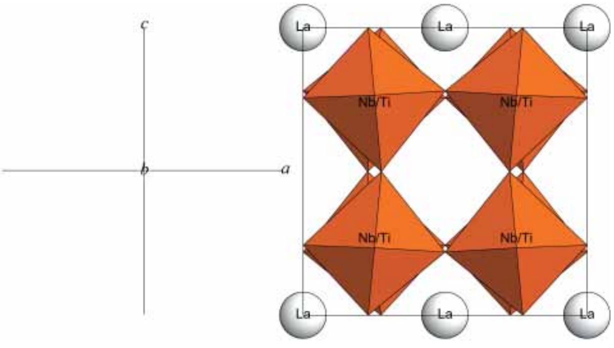


Figure 8. Projection of the unit cell content of compound **3** along its *b* axis.

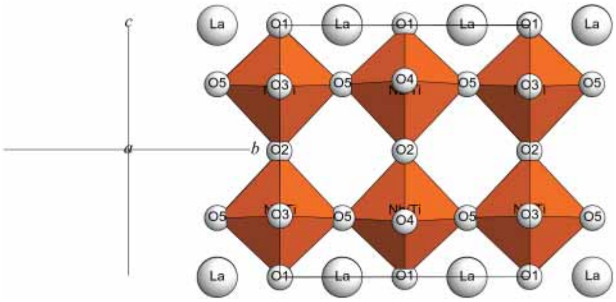


Figure 9. Projection of the structure of compound **3** along its *a* axis.

each pair sharing a common edge. Such a pair is connected *via* common corners to two others, one below and one above it, forming infinite chains that run parallel to *b* axis. These chains are connected through the remaining corners into a three dimensional framework with tunnels along the *b* axis, where La^{3+} cations are situated. Each La atom is surrounded by eight O atoms at distances from 2.457(6) to 2.543(6) Å. The Nb/Ti–O distances are from 1.893(6) to 2.144(6) Å.

The structure of compound **3** is shown in Figures 8 and 9. As expected, it is basically very similar to that of the defect perovskite structure of La$_{1/3}$NbO$_3$,[28] consisting of corner sharing, tilted and distorted Nb/TiO$_6$ octahedra and La^{3+} cations surrounded by twelve O^{2-} anions at distances from 2.625(13) to 2.901(11) Å. On the other hand, replacement of 11.1 % of Nb^{5+} sites by Ti^{4+} and enlargement of the occupancy of La^{3+} from 66.7 % to 74.1 % cause small changes in the unit cell parameters. Cell edges *a* and *b* are 0.0152 Å shorter while *c* is 0.0098 Å longer in compound **3** relative to those in La$_{1/3}$NbO$_3$.[28] The ionic radius[61] of Ti^{4+} is 0.035 Å smaller than that of Nb^{5+}, which should contribute to the contraction of the unit cell of compound **3** relative to that of La$_{1/3}$NbO$_3$, while the larger amount of La^{3+} should have the opposite, sterically still isotropic effect. Explanation for the above mentioned anisotropic change, where only the *c* cell edge is enlarged in solid solution, could be that the larger amount of lanthanum increases the repulsion between La^{3+} and Nb^{+5}/Ti^{+4}, which causes the larger shift of Nb/Ti sites along the *c* axis toward the layer consisting of O atoms (O2) and cations vacancies and away from the parallel layer consisting of La and O atoms (O1). This shift of Nb/Ti sites, which is 0.007 Å larger in compound **3** than in La$_{1/3}$NbO$_3$, has an additional effect also on Nb/Ti–O interatomic distances. The elongation of Nb/Ti–O(1) and shortening of Nb/Ti–O(2) distances 2.092(2) and 1.888(2) Å, respectively, relative to the remaining four Nb/Ti–O distances (from 1.968(5) to 1.971(6)) is larger in compound **3** than in La$_{1/3}$NbO$_3$.

CONCLUSION

The methods of structure determination from powder diffraction, which have been intensively developed during the last twenty years, have been successfully applied also for ceramic materials. This is especially true of the reciprocal space methods (Patterson and Direct methods). On the other hand, there are also new perspectives for this kind of inorganic compounds also in the field of real space methods. Nevertheless, structures of new compounds, belonging to ceramics, can still be determined also in the classical-empirical way, if the compounds crystallize in a known structural type. We have demonstrated this on three compounds from the ternary system of La_2O_3–Nb_2O_5–TiO_2.

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REFERENCES

1. A. R. West, *Solid State Chemistry and Its Applications*, John Wiley & Sons, Chichester, 1989, pp. 36–40.
2. W. I. F. David, K. Shankland, L. B. McCusker, and Ch. Bearlocher, *Structure Determination from Powder Diffraction Data*, Oxford University Press, Oxford, 2002, pp. 1–11.
3. H. M. Rietveld, *J. Appl. Crystallogr.* **2** (1969) 65–71.
4. Powder Diffraction Database – PDF, International Centre for Diffraction Data – ICDD, 12 Campus Boulevard, Newtown Square, PA 19073–3273 USA.
5. Inorganic Crystal Structure Database – ICSD, FIZ Karlsruhe, PO Box 2465
D–76012 Karlsruhe, Germany.
6. V. Favre-Nicolin and R. Černý, *J. Appl. Crystallogr.* **35** (2002) 734–743.
7. A. Meden, *Croat. Chem. Acta* **71** (1998) 615–633.
8. G. S. Pawley, *J. Appl. Crystallogr.* **14** (1981) 356–361.
9. A. LeBail, H. Durray, and J. L. Fourquet, *Mat. Res. Bull.* **23** (1988) 447–452.
10. A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, M. C. Burla, and G. Polidori, *J. Appl. Crystallogr.* **28** (1995) 738–744.
11. P. Main, L. Lessinger, M. M. Woolfson, G. Germain, and J. P. Declercq, *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data,* University of York, England, and Louvain, Belgium, 1977.
12. G. M. Sheldrick, SHELXS97, University of Götingen, Germany, 1997.
13. A. Altomare, M. C. Burla, M. Camalli, B. Carrozzini, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Rizzi, *J. Appl. Crystallogr.* **32** (1999) 339–340.
14. W. I. F. David, K. Shankland, L. B. McCusker, and Ch. Bearlocher, *Structure Determination from Powder Diffraction Data*, Oxford University Press, Oxford, 2002, pp. 309–314.
15. K. D. M. Harris, M. Tremyane, P. Lightfoot, and P. G. Bruce, *J. Am. Chem. Soc.* **116** (1994) 3543–3547.
16. Y. G. Andreev, G. S. MacGlashan, and P. G. Bruce, *Phys. Rev. B, Condens. Matter* **55** (1997) 12011–12017.
17. J. M. Newsam, M. W. Deem, and C. M. Freeman, *Accuracy in Powder Diffraction II,* NIST Special Publ. No. 846, 1992, pp. 80–91.
18. M. Falcioni and M. W. Deem, *J. Chem. Phys.* **110** (1999) 1754–1766.
19. B. M. Kariuki, H. Serrano-Gonzales, R. L. Johnston, and K. D. M. Harris, *Chem. Phys. Lett.* **280** (1997) 189–195.
20. K. Shankland, W. I. F. David, and T. Csoka, *Z. Kristallogr.* **212** (1997) 550–552.
21. Topas 2.1: General Profile and Structure Analysis Software for Powder Diffraction Data, Bruker AXS, Karlsruhe, Germany, 2003.
22. V. Paul-Boncour, Y. M. Filipek, A. Percheron-Guégan, I. Marchuk, and J. Peilassek, *J. Alloys Compd.* **58** (2001) 317–318.
23. L. Guénée, V. Favre-Nicolin, and K. Yvon, *J. Alloys Compd.* **348** (2003) 129–137.
24. G. Renaudin, L. Guénée, and K. Yvon, *J. Alloys Compd.* **350** (2003) 145–150.
25. R. Černý, I. Yu. Zavaliy, and I. V. Koval'chuk, *J. Alloys Compd.* Submitted.
26. I. R. Evans, J. A. K. Howard, R. L. Withers, and J. S. O. Evans, *Chem. Commun.* (2001) 1984–1985.
27. Y. Laligant, A. Le Bail, and F. Goutnoire, *J. Solid State Chem.* **159** (2001) 223–227.
28. R. A. Dilanian, A. Yamamoto, F. Izumi and T. Kamiyama, *Mol. Crys. Liq. Cryst.* **341** (2000) 1029–1034.
29. L. Carrillo, M. E. Villafuerte-Castrejon, G. Gonzalez, L. E. Sansores, L. Bucio, J. Duque, and R. Pomes, *J. Mater. Sci.* **35** (2000) 3047–3052.
30. C. Bridges, J. E. Greedan, and J. Barbier, *Acta Crystallogr., Sect. B* **56** (2000) 183–188.
31. C. Grenthe, A. Guagliardi, M. Sundberg, and P. Werner, *Acta Crystallogr., Sect. B* **57** (2001) 13–19.
32. M. Gemmi, L. Righi, G. Calestani, A. Migliori, A. Speghini, M. Santarosa, and M. Bettinelli, *Ultramicroscopy* **84** (2000) 133–142.
33. A. R. West, *Solid State Chemistry and its Applications*, John Wiley & Sons, Chichester, 1989, p. 553.
34. T. E. Weirich, R. Ramlau, A. Simon, S. Hovmoller, and X. D. Zou, *Nature* **382** (1996) 144–146.
35. J. Gjonnes, V. Hansen, B. S. Berg, P. Runde, Y. F. Cheng, K. Gjonnes, D. L. Dorset, and C. J. Gilmore, *Acta Crystallogr., Sect. B* **54** (1998) 306–319.
36. S. Marzullo and E. N. Bunting, *J. Am. Ceram. Soc.* **41** (1958) 40–41.
37. J. B. MacChesney and H. A. Sauer, *J. Am. Ceram. Soc.* **45** (1962) 416–422.
38. P. A. Fuierer and R. E. Newnham, *J. Am. Ceram. Soc.* **74** (1991) 2876–2881.
39. S. D. Škapin, D. Kolar, and D. Suvorov, *J. Eur. Ceram. Soc.* **20** (2000) 1179–1185.
40. M. Yokoyama, T. Ota, I. Yamai, and J. Takahashi, *J. Cryst. Growth* **96** (1989) 490–496.
41. S. D. Škapin, D. Kolar, and D. Suvorov, *J. Am. Ceram. Soc.* **76** (1993) 2359–2362.
42. R. Ali, M. Yashima, M. Yoshimura, and H. Yoshioka, *J. Am. Ceram. Soc.* **84** (2001) 468–470.
43. D. Kolar, S. D. Škapin, D. Suvorov, and M. Valant, *Proceedings of the Ninth International Conference on High Temperature Materials Chemistry,* (Penn State, University Park, PA, May 19–23, 1997), Vol. IX, The Electrochemical Society, Pennington, 1997, pp. 109–115.
44. D. Suvorov, M. Valant, S. D. Škapin, and D. Kolar, *J. Mater. Sci.* **33** (1998) 85–89.
45. P. N. Iyer and A. J. Smith, *Acta Crystallogr.* **23** (1967) 740–746.

46. (a) D. Fauquier and M. Gasperin, *Bull. Soc Fr. Mineral. Cristal.* **93** (1970) 258. (b) ICSD collection code: 23509, PDF card number: 73-1059.
47. R. Ali, M. Yashima, M. Tanaka, H. Yoshioka, T. Mori, and S. Sasaki, *J. Solid State Chem.* **164** (2002) 51–59.
48. H. Yoshioka, *J. Am. Ceram. Soc.* **85** (2002) 1339–1341.
49. M. Yashima, M. Mori, T. Kamiyama, K. Oikawa, A. Hoshikawa, S. Torii, K. Saitoh, and K. Tsuda, *Chem. Phys. Lett.* **375** (2003) 240–246.
50. (a) A. Sych and V. Klenus, *Inorg. Mater.* **9** (1973) 1081. (b) PDF card number: 31-0672.
51. (a) Frank-Kamenetsky, University of Leningrad, Russia, personal communication (1968). (b) PDF card number: 20-1367.
52. Natl. Bur. Stand. (U.S.) Monogr. 25,3,37 (1964); PDF card number: 15-0872.
53. O. Loye, P. Laruelle, and A. Harari, *Comptes Rendus Hebdomadaires des Seances de l'Academie des Sciences, Serie C, Sciences Chimiques* **266** (1968) 454–456.
54. A. F. Wells, *Structural Inorganic Chemistry,* 5th ed., Oxford University Press, Oxford, 1986, pp. 182–183.
55. (a) V. K. Trunov, I. M. Averina, A. A. Evdokimov, and A. M. Frolov, *Kristallografiya,* **26** (1981) 189–191. (b) *Vestnik Moskovskogo Universiteta, Khimiya* (1968) 55.
56. R. W. Cheary and A. A. Coelho, *J. Appl. Crystallogr.* **25** (1992) 109–121.
57. R. W. Cheary and A. A. Coelho, *J. Appl. Crystallogr.* **31** (1998) 851–861.
58. R. W. Cheary and A. A. Coelho, *J. Appl. Crystallogr.* **31** (1998) 862–868.
59. A. A. Coelho and R. W. Cheary, *Comput. Phys. Commun.* **104** (1997) 15–22.
60. A. F. Wells, *Structural Inorganic Chemistry,* 5th ed., Oxford University Press, Oxford, 1986, pp. 635–636.
61. D. Shannon, *Acta Crystallogr. Sect. A* **32** (1976) 751–767.
62. The lists are made with the help of web page by Le Bail, http://www.cristal.org/iniref.html
63. M. S. Lehmann, A. Norlund Christensen, H. Fjellvag, R. Feidenhans'l, and M. Nielsen, *J. Appl. Crystallogr.* **20** (1987) 123–129.
64. S. J. Hibble, A. K. Cheetham, A. R. L. Bogle, H. R. Wakerley, and D. E. Cox, *J. Am. Chem. Soc.* **110** (1988) 3295–3296.
65. A. Le Bail, H. Duroy, and J. L. Fourquet, *Mat. Res. Bull.* **23** (1988) 447–452.
66. Y. Laligant, A. Le Bail, and G. Ferey, *J. Solid State Chem.* **81** (1989) 58–64.
67. A. Le Bail and M.-A. Lafontaine, *Eur. J. Solid State Inorg. Chem.* **27** (1990) 671–680.
68. P. Norby, A. Norlund Christensen, H. Fjellvag, and M. Nielsen, *J. Solid State Chem.* **94** (1991) 281–293.
69. P. Lightfoot, J. A. Hriljac, S. Pei, Y. Zheng, A. W. Mitchell, D. R. Richards, B. Dabrowski, J. D. Jorgensen, and D. G. Hinks, *J. Solid State Chem.* **92** (1991) 473–479.
70. Y. Laligant, *Eur. J. Solid State Inorg. Chem.* **29** (1992) 239–247.
71. Y. Laligant and A. Le Bail, *Eur. J. Solid State Inorg. Chem.* **30** (1993) 689–698.
72. R. E. Morris, J. J. Owen, J. K. Stalick, and A. K. Cheetham, *J. Solid State Chem.* **111** (1994) 52–57.
73. P. Lightfoot, J. B. Thomson, F. J. Little, and P. G. Bruce, *J. Mater. Chem.* **4** (1994) 167–169.
74. J.-C. Champarnaud-Mesjard, B. Frit, A. Aftati, and M. El Farissi, *Eur. J. Solid State Inorg. Chem.* **31** (1994) 473–486.
75. R. J. Balsys and R. L. Davis, *Solid State Ionics* **69** (1994) 69–74.
76. A. Le Bail, L. Permer and Y. Laligant, *Eur. J. Solid State Inorg. Chem.* **32** (1995) 883–892.
77. Y. Laligant, L. Permer, and A. Le Bail, *Eur. J. Solid State Inorg. Chem* **32** (1995) 325–334.
78. W. T. A. Harrison, S. L. Hegwood, and A. J. Jacobson, *J. Chem. Soc. Chem. Commun.* **19** (1995) 1953–1954.
79. J.-C. Champarnaud-Mesjard, B. Frit, A. Aftati, and M. El Farissi, *Eur. J. Solid State Inorg. Chem.* **32** (1995) 493–504.
80. N. Tancret, S. Obbade, N. Bettahar, and F. Abraham, *J. Solid State Chem.* **124** (1996) 309–318.
81. P. M. Woodward, A. W. Sleight, and T. Vogt, *J. Solid State Chem.* **131** (1997) 9–17.
82. L. Permer and Y. Laligant, *Eur. J. Solid State Inorg. Chem.* **34** (1997) 41–52.
83. I. Radosavljevic, J. S. O. Evans, and A. W. Sleight, *J. Solid State Chem.* **137** (1998) 143–147.
84. K. Knorr, P. Jakubus, G. Dabrowska, and M. Kursawa, *Eur. J. Solid State Inorg. Chem.* **35** (1998) 519–530.
85. P. Pertierra, M. A. Salvado, S. Garcia-Granda, C. Trabajo, J. R. Garcia, A. I. Bortun, and A. Clearfield, *J. Solid State Chem.* **148** (1999) 41–49.
86. S. Kubota, H. Yamane, and M. Shimada, *Acta Crystallogr., Sect. C* **55** (1999) 14–17.
87. F. Dubois, F. Goutenoire, Y. Laligant, E. Suard, and P. Lacorre, *J. Solid State Chem.* **159** (2001) 228–233.
88. M. I. Gomez, G. Lucotti, J. A. de Moran, P. J. Aymonino, S. Pagola, P. Stephens, and R. E. Carbonio, *J. Solid State Chem.* **160** (2001) 17–24.
89. A. M. Krogh Andersen and S. Stefan Carlson, *Acta Crystallogr., Sect. B* **57** (2001) 20–26.
90. R. E. Dinnebier, R. M. Ibberson, H. Ehrenberg, and M. Jansen, *J. Solid State Chem.* **163** (2002) 332–339.
91. J. Grins and P. E. Werner, *Acta. Chem. Scand.* **43** (1989) 11–14.
92. A. Jouanneaux, O. Joubert, A. N. Fitch, and M. Ganne, *Mat. Res. Bull.* **26** (1991) 973–982.
93. J. A. Hriljac, J. B. Parise, G. H. Kwei, and K. B. Schwartz, *J. Phys. Chem. Solids* **52** (1991) 1273–1279.
94. A. Jouanneaux, O. Joubert, M. Evain, and M. Ganne, *Powder Diffraction* **7** (1992) 206–211.
95. W. G. Mumme, *J. Solid State Chem.* **105** (1993) 528–534.
96. M. Zocchi, I. Natali Sora, L. E. Depero, and R. S. Roth, *J. Solid State Chem.* **104** (1993) 391–396.
97. F. Goutenoire, V. Caignaert, M. Hervieu, C. Michel, and B. Raveau, *J. Solid State Chem.* **114** (1995) 428–434.
98. F. Goutenoire, V. Caignaert, M. Hervieu, C. Michel, and B. Raveau, *J. Solid State Chem.* **115** (1995) 508–513.
99. F. Goutenoire, V. Caignaert, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **119** (1995) 134–141.
100. E. Grey, L. M. D. Cranswick, C. Li, L. A. Bursill, and J. L. Peng, *J. Solid State Chem.* **138** (1998) 74–86.

SAŽETAK

Rješavanje strukturnih problema keramičkih materijala

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Prikazane su metode za određivanje kristalne strukture iz podataka dobivenih difrakcijom na prahu s posebnim naglaskom na primjenu za tehničku keramiku. Opisane su, također, eksperimentalne tehnike koje se služe i drugim pristupima osim laboratorijskih X-zraka, na pr. sinhrotronskim zračenjem, neutronskim i elektronskim snopovima. Kao ilustrativni primjer opisana su određivanja kristalnih struktura spojeva $LaNbTiO_6$ (**1**), $La_{0,462}Nb_{0,614}Ti_{0,386}O_3$ (**2**) i $La_{0,37}Nb_{0,889}Ti_{0,111}O_3$ (**3**) iz ternarnoga sistema La_2O_3–Nb_2O_5–TiO_2.