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Electron microscopy and structural studies of $Nd_{1/3}NbO_3$

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Abstract

The crystal structure of the deficient perovskite $Nd_{1/3}NbO_3$ has been determined at room temperature, using electron microscopy observations and X-ray powder diffraction data. Electron diffraction study and HRTEM images evidence the doubling of *a* and *b* parameters and confirm one of the *c*-parameter with respect to perovskite unit cell. The structure refinement has been carried out using the orthorhombic *Cmmm* space group. The Nd^{3+} cations occupy randomly and alternatively the (00l) planes and Nb^{5+} cations distorted octahedral sites. This structure is characterized by the presence of empty Nd^{3+} sites in every second layer and the tilting of the octahedral sites around the *b*-axis. In addition, electron diffraction patterns exhibit weak additional diffuse reflections, which supposes some ordering of the Nd vacancies. ***To cite this article: S. Roudeau et al., C. R. Chimie 11 (2008).***

Résumé

La structure cristalline de la perovskite $Nd_{1/3}NbO_3$ lacunaire en néodyme a été déterminée à température ambiante sur la base de données de microscopie électronique et de diffraction X. Les clichés de diffraction électronique ainsi que les images de haute résolution montrent un doublement des paramètres *a* et *b* et confirment celui du paramètre *c*. L'affinement de la structure a été réalisé avec le groupe spatial *Cmmm*. Les cations Nd^{3+} occupent statistiquement et alternativement les plans (00l) et les cations Nb^{5+} des sites octaédriques distordus. La structure est caractérisée par la présence de sites vides de Nd^{3+} dans un plan sur deux selon l'axe *c* et par une inclinaison des octaèdres autour de l'axe *b*. De faibles réflexions diffuses sont visibles dans les clichés de diffraction électronique, qui pourraient être dues à un ordre local des lacunes de néodyme. ***Pour citer cet article : S. Roudeau et al., C. R. Chimie 11 (2008).***

Keywords: Perovskite, Niobate; Crystal structure; Electron microscopy; Cation ordering

Mots-clés : Perovskite, Niobiate ; Structure cristalline ; Microscopie électronique, Ordre cationique

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1. Introduction

The ideal perovskite has the general formula ABX_3, where the A-site cations are typically larger than the B-site ones and similar in size to the X-site anions. In this structure, the A cations are surrounded by 12 anions in cubo-octahedral coordination and the B cations are surrounded by 6 anions in octahedral coordination. The ideal structure adopts the cubic space group $Pm\bar{3}m$ [1].

One of the most important characteristics of perovskite-related structures is their compositional flexibility. This structure can tolerate anionic non-stoichiometry in the X-site as well as cationic deficiency in the A-site. Cation-deficient perovskite-type oxides $A_{1-x}BO_3$ have been studied for a number of years. Compounds with B = W, Mo or Re are named "bronzes" and A (usually alkali metal) occupies a random position; those with Ti, Nb or Ta, namely "non-stoichiometric perovskites", exhibit some ordering of A cations. Their structure consists of the framework of BO_6 octahedra with partially occupied layers of A-site cations alternating with A-vacant layers along the *c*-axis resulting in a doubling of the perovskite cell along the *c*-axis (Fig. 1). Several $A_{1-x}BO_3$ perovskite oxides do exist, such as $Ln_{2/3}TiO_3$ [2,3], $Ln_{1/3}BO_3$ (B = Nb, Ta) [4–9] or $Th_{1/4}NbO_3$ [10]. For this latter compound, an additional long-range ordering between Th atoms and vacancies, giving rise to modulation or localized diffusion, has been detected by electron and X-ray diffraction. This kind of material has also been shown to exhibit interesting properties as electrodes for the Li ion insertion reactions in batteries or for their dielectric behavior and magnetic response [11–14].

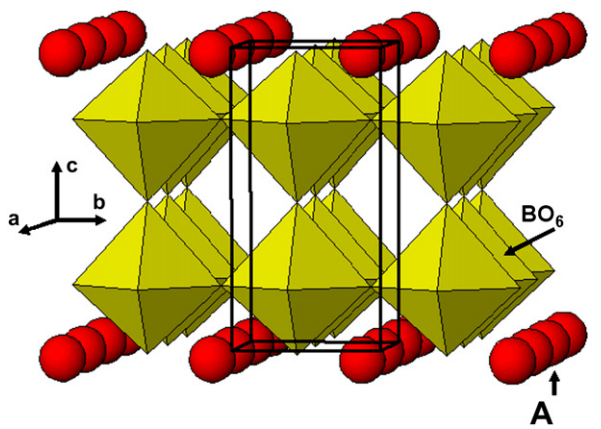

Fig. 1. Idealized structure of $A_{1-x}BO_3$: B = Ti ($x = 0.33$) or Nb ($x = 0.66$) showing the half (00l) empty planes and half (001) partially filled planes.

The crystal structure of $Nd_{1/3}NbO_3$ was first reported by Iyer et al. [9] as isotype of β-$La_{1/3}NbO_3$, in which the lanthanide ions order into alternate (00l) planes, doubling the *c*-parameter. $Nd_{1/3}NbO_3$ crystallizes in the orthorhombic space group *Pmmm* with cell parameters $a = 3.878$ Å, $b = 3.907$ Å and $c = 7.840$ Å (Table 1) at room temperature. Later on, Carrillo et al. [15], using electron microscopy, observed a superstructure in β-$La_{1/3}NbO_3$ ($2a \times 2b \times c$). Nevertheless, their X-ray diffraction data, even with a careful analysis, did not reveal any features which could be related to the presence of the superstructure observed by electron microscopy. Thus, they interpreted the superstructure as resulting from distorted octahedra on the basis of simulation of the X-ray diffraction patterns.

The aim of the present work is to characterize $Nd_{1/3}NbO_3$ using XRD (Rietveld refinement) and electron microscopy observations in order to establish whether the superstructure observed in β-$La_{1/3}NbO_3$ is present or not in this compound.

2. Experimental

Powder of $Nd_{1/3}NbO_3$ was obtained by solid-state reaction. The starting materials Nd_2O_3 and Nb_2O_5 oxides (Aldrich, purity 99.9%) were first dried in air, at 1000 °C, for 24 h. A stoichiometric mixture of these oxides was ground with ethanol in an agate mortar and then heated in an alumina crucible at 1100 °C in air for 10 h, and, after intermediate regrinding, at 1300 °C for 36 h, in air.

The XRD pattern of $Nd_{1/3}NbO_3$ was recorded at room temperature on a Philip X'pert Pro powder diffractometer in the Bragg–Brentano geometry with a back monochromator, using Cu $K\alpha_1$ radiations ($\lambda = 1.5406$ Å). The data collection was performed in the 6–130° 2θ range with a 0.0080° step, using an X'celerator detector (linear PSD covering 2.122 mm).

The diffraction data were analyzed using the Rietveld technique as implemented in the Fullprof program

Table 1
Structural data of $Nd_{1/3}NbO_3$ from Iyer et al. [9]

$Nd_{1/3}NbO_3$	
Crystal system	Orthorhombic
Space group	*Pmmm*
Z	8
Lattice parameters (Å)	$a = 3.8807$ (1) $b = 3.9067$ (1) $c = 7.8365$ (1) $\alpha = \beta = \gamma = 90$ °C
Volume (Å^3)	118.8