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# Electronic structure of layered titanate $Nd_2Ti_2O_7$

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ABSTRACT

The electronic structure of the binary titanate $Nd_2Ti_2O_7$ has been studied by X-ray photoelectron spectroscopy (XPS). Spectral features of the valence band and all constituent element core levels have been considered. The Auger parameters of titanium and oxygen in $Nd_2Ti_2O_7$ are determined as $\alpha_{Ti} = 873.5$ and $\alpha_O = 1042.2$ eV. Chemical bonding effects have been discussed with the binding energies differences $\Delta_{Ti}$ = (BE O 1s – BE Ti $2p_{3/2}$) = 71.5 eV and $\Delta_{Nd}$ = (BE Nd $3d_{5/2}$ – BE O 1s) = 452.5 eV as key parameters in comparison with those in other titanium- and neodymium-bearing oxides.



## 1. Introduction

Neodymium dititanate, $Nd_2Ti_2O_7$ (NTO), is a member of small family of rare earth titanates $Ln_2Ti_2O_7$ (Ln = La, Ce, Pr, Nd) with ferroelectric properties [1]. At room temperature NTO is monoclinic, space group $P2_1$, and has a layered structure formed by infinite layers of strongly distorted $TiO_6$ octahedra [2]. The crystal structure of NTO is shown in Fig. 1. There are eight sites for Ti atoms with Ti–O distances ranging from 182 to 223 pm. Nd atoms are positioned in eight sites, all coordinated by 12 oxygens with Nd–O distances in the range 240–385 pm. Because of eight different sites for $Nd^{3+}$ ions, eight sites for $Ti^{4+}$ ions and considerable variations of Nd–O and Ti–O distances in the crystal lattice, $Nd_2Ti_2O_7$ shows a great potential for solid solution formation with possible substitution in Nd or Ti positions. As to physical properties, $Nd_2Ti_2O_7$ is characterized by an extremely high Curie temperature $T_C > 1500$ °C, spontaneous polarization $P_s = 9$ μC/cm$^2$, high permittivity $\varepsilon = 31$–47 [1,3–5] and high piezoelectric properties [1,6] that holds promises for using this compound for the manufacture of ferroelectric random access memory (FRAM) elements [7–11]. Thermal stability up to $T \sim 1400$ °C and low dielectric losses open the way for a wide use of NTO as a key component in the fabrication of microwave ceramics and nanocomposites [12–22]. High refractive indices $n_a = 2.15$, $n_b = 2.27$ and $n_c = 2.23$ ($\lambda = 526.5$ nm) and a reasonable level of nonlinear optical susceptibility were measured for NTO [4,23–25]. NTO is a multiferroic and a magnetochiral effect has been observed recently in this compound [12,26,27].

Recently, much attention has been paid to photocatalytic water splitting with the help of layered perovskite-type oxides and $Nd_2Ti_2O_7$ is classified as an effective compound for this surface chemical reaction [28,29]. To relate the photocatalytic activity of NTO to electronic parameters, the forbidden band gap energy $E_g = 3.65$ eV was estimated with spectroscopic methods and the valence band structure was measured with X-ray photoelectron spectroscopy (XPS) [29]. A model has been proposed that speculates that the variation of $E_g$ values and valence band features in $Ln_2Ti_2O_7$ oxides is induced by the variation of the energy position of Ln 4f states [29]. The present study aims at producing a detailed observation of the electronic structure of NTO with XPS. Then, chemical bonding effects will be considered for NTO in comparison with related titanates such as $Ln_2Ti_2O_7$, Ln = La, Gd, and $Y_2Ti_2O_7$, because a previously published study based on binding energy values of O 1s and Ti$2p_{3/2}$ core levels in titanates reveals specific features on the relationship between electronic and structural parameters of Ti–O bonds [30].

## 2. Experimental

The starting reagents for sample preparation consisted in high purity oxide powders. After grinding in an agate mortar, the mixture with $Nd_2Ti_2O_7$ stoichiometry was calcined at 850 °C for 60 h and then reacted at 1100 °C for a total of 300 h (60 h + 90 h + 150 h) with intermediate grinding steps. The last heat treatment was performed without compaction, resulting in loosely agglomerated powders. This avoided the introduction of crystal lattice strain through grinding. XRD patterns were recorded after each heat treatment with a STOE diffractometer using Cu Kα radiation. Cell parameter calculations were

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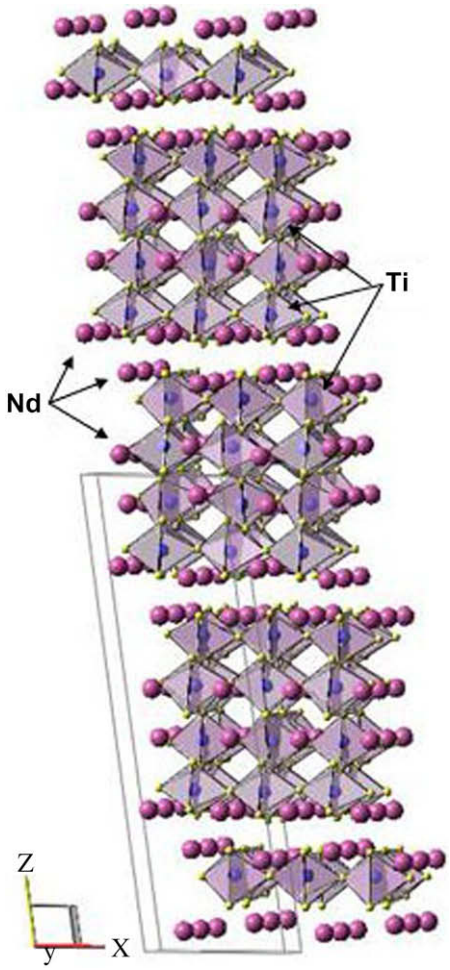


**Fig. 1.** Crystal structure of $Nd_2Ti_2O_7$. Large spheres and octahedra represent Nd and $TiO_6$ octahedra, respectively. The unit cell is outlined.

performed by a least square fit method. Micromorphology of the oxide particles was observed by means of scanning electron microscopy (SEM) using a LEO 1430 device at electron energy 10 keV. Chemical composition has been measured with electron probe micro-analysis (EPMA). Residual stress has been evaluated from X-ray diffraction line broadening by means of the single-line method described by Keijser et al. [31], using a silicon standard powder for subtracting the instrumental contribution to line broadening.

X-ray photoemission spectra were obtained with a MAC-2 (RIBER) analyzer using non-monochromatic Al Kα radiation (1486.6 eV) with a power of 240 W. This X-ray source was chosen to minimize the effects of superposition of photoelectron and Auger lines of constituent elements. The diameter of the X-ray beam was ~5 mm. The energy resolution of the instrument was chosen to be 0.7 eV, in order to have sufficiently small broadening of natural core level lines together with reasonable signal-noise ratio. Under these conditions the observed full width at half maximum (FWHM) of the Au $4f_{7/2}$ line was 1.31 eV. The binding energy scale was calibrated in reference to the Cu $3p_{3/2}$ (75.1 eV) and Cu $2p_{3/2}$ (932.7 eV) lines, giving an accuracy of 0.1 eV in any peak energy position determination. Photoelectron energy drift due to charging effects was taken into account in reference to the position of the C 1s (284.6 eV) line generated by adventitious carbon present on the surface of the powder as-inserted into the vacuum chamber.

## 3. Results and discussion

The final product of high temperature synthesis was of purple color. The micromorphology of the powder is shown in Fig. 2. Regular particles with characteristic dimensions ~1 μm are found. It is evident that the heat treatment time of 300 h used for solid state reaction was long enough for the $Nd_2Ti_2O_7$ grains to be well coalesced due to diffusion intergrowth. Hence, the crystallinity of the $Nd_2Ti_2O_7$ oxide is very good as confirmed by the XRD pattern shown in Fig. 3S. All the peaks were attributed to the $Nd_2Ti_2O_7$ phase. The EPMA analysis shows the presence of only Nd, Ti and O elements in the synthesized oxide with ratios Nd:Ti = 1:0.99 and O:Ti = 2.8 that are in good agreement with the nominal composition of $Nd_2Ti_2O_7$. The residual stress ($e$) was evaluated from several X-ray reflections in the angular range $25° < 2\theta < 45°$. The results are in the interval $0.0002 \pm 0.0001 \leqslant e \leqslant 0.0009 \pm 0.0002$ without obvious dependence on the crystallographic orientation. The relatively large uncertainty results form the fact that the integral width of the $Nd_2Ti_2O_7$ sample's reflections is quite close to that of the Si(111) and Si(220) reflections used for determining the instrumental contribution to peak broadening. The fairly low $e$ values indicate that the bond length and thus binding energies are not affected by residual stress.

The survey photoelectron spectrum is shown in Fig. 3. All spectral features, except one, were attributed to constituent element

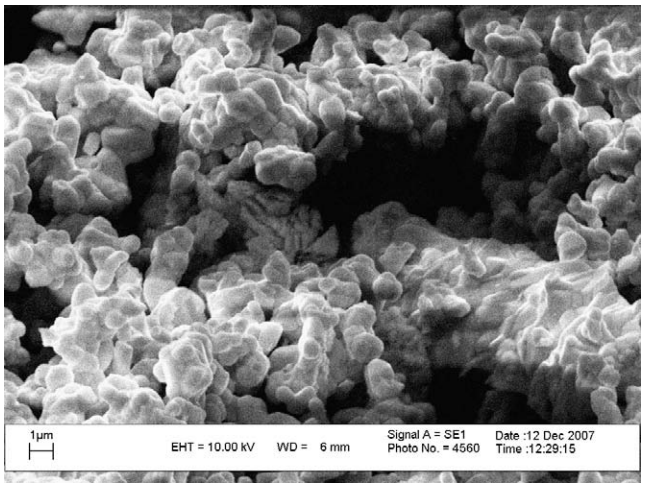


**Fig. 2.** SEM image of the $Nd_2Ti_2O_7$ powder.

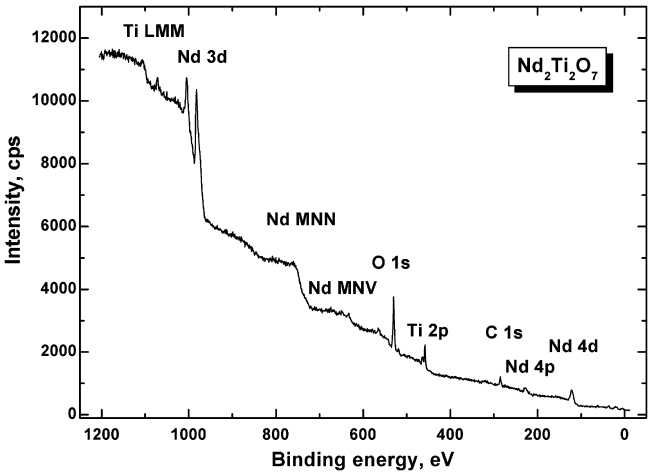


**Fig. 3.** Survey X-ray photoemission spectrum of $Nd_2Ti_2O_7$.