

Comparative Crystallographic Study of La₂NiTiO₆ Double Perovskite Structure using Crystallographic Software's

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Abstract: Among multifunctional La₂BB'O₆ (B/B' are transition metals) double perovskites, La₂NiTiO₆ has recently received significant attention due to its rich physics and prospects in technological applications. In the present study, bulk La₂NiTiO₆ double perovskite sample has been synthesized using sol-gel method. Rietveld profile analysis of the low temperature X-ray powder diffraction data of the sample at the room temperature have emphasized on the formation of single phase monoclinic (P21/n space group) La₂NiTiO₆ compound. The lattice parameter and atomic positions have computed with the help of different crystallographic software's using FULLPROF & Vesta structure simulation program, and compare these data with SPuDS structure prediction simulation software's data.

INTRODUCTION

The crystal structures and various properties of perovskite related materials with the double formula A₂BB'O₆ depend upon the size and electronic structure of the transition metal cations B and B'. If the two species are of similar size and charge they are likely to be distributed over the 6-coordinate sites in a disordered manner; otherwise they arrange themselves in an alternate manner thus increasing the size of the unit cell. In either case the special physical properties are strongly related to charge ordering phenomena. Perovskite-type oxides of the transition elements have been extensively studied since they present interesting magnetic and transport properties. Famous examples are superconducting mixed-valent copper oxides and the mixed-valent manganese perovskites exhibiting giant magnetoresistance.[1] La₂NiTiO₆ (LNTO) double perovskites features as a high-spin paramagnet with the peculiar electronic structure: a half-filled e_g manifold at the Fermi level which is extremely narrow and uncommonly well separated from any other band. The origin of this lies in the isotropic reduction of the hoppings in all three spatial directions, something hardly possible to achieve artificially but that nature does very effectively. This class of d₈-d₀ double perovskites can open new directions in oxide engineering: by considering also heavier elements of the Ni group and upon splitting the e_g and s by heterostructuring or strain a correlation-driven band inversion can be realized, as in recent theoretical proposals for interacting topological insulators. The low value of the Neel temperature $T_N \sim 253K$ in LNTO has the interesting consequence that its para-magnetic mott insulating state can be observed in an unusually extended range of temperatures [2].

In the present work, herein, we report the findings of X-ray powder diffraction analysis as the structural properties of the synthesized sample La₂NiTiO₆ prepared by sol-gel process followed by sintering at high temperature. It is a known fact that SPuDS generates structures using computational tools for hypothetical compositions of those compounds where structural data are not available. While FULLPROF [3] and VESTA's [4] computed results provide a computed results of the synthesized system using its experimentally refined structural parameter. We compare the obtained data via FULLPROF and VESTA with the SPuDS [5] software computed data to check the reliability of the software along with the synthesis and structural study of the prepared La₂NiTiO₆ compound.

EXPERIMENTAL

LNTO Samples were prepared using the citrate route in order to increase the homogeneity of the starting mixture of the elements. The starting salts were $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, purity 99.99%), $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Alfa Aesar, 99.99085% metal basis). The raw powders, in stoichiometric ratio, were mixed together in distilled water under constant stirring. Titanium (IV) butoxide (Sigma- Aldrich, 97.0 wt %) was thereafter added to the solution, whereupon a white precipitate of hydrated titanium oxide formed. To this precursor mixture, then a fixed amount of anhydrous citric acid in deionised water corresponded to three times the total positive charge of the cations was added to the solution as a complex binder to get a well dispersed mixture of the elements in the precursor gel. The resulting clear solution was kept under constant magnetic stirring at 80°C for 6 h until a viscous gel formed. The gel was further heated in air to 900°C at a rate of $5^\circ\text{C}/\text{min}$ and held at 900°C for 2 h in order to burn off the organic parts and to produce fluffy black powders. Black powder was ground into fine powder using a pestle and mortar. The amorphous material thus obtained was pressed and fired in air at 1350°C for 24 hours. The phase characterization of these materials was carried out by powder X-ray diffraction technique (Bruker D2 Phaser X-ray diffractometer) with $\text{Cu K}\alpha$ radiation having wavelength of 1.54 \AA . The scanning was done in the region of 2θ from 10° to 90° . While, in order to optimize the type of band-to-band transition in the synthesized sample, the optical absorbance spectra recorded in the wave length range (200-1100) nm.

RESULT AND DISCUSSION

The sample synthesized using sol gel method and the XRD data was refined by the Rietveld method by using the FULLPROF refinement program. A pseudo-voight function was chosen to generate the line shape of the diffraction peaks. No regions were excluded in the refinement. The parameters that were refined in the final runs are: scale factor, background positions, Ti at $2d(1/2, 0, 0)$ positions, Ni at $2c(0, 1/2, 0)$, La atoms and the all the three types of oxygen atoms at $4e(x, y, z)$ sites for profile fitting. Finally a monoclinic structure (space group $P2_1/n$) was used to analyze the diffraction pattern which does permit ordering of Ni^{2+} and Ti^{4+} cations over the 6-coordinate sites of the structure, there are no secondary phases or impurities were observed. The monoclinic structure is the preferred structure for rocksalt type ordering of $\text{La}_2^{3+}\text{Ni}^{2+}\text{Ti}^{4+}\text{O}_6^{2-}$ double perovskites with t values lower than 0.93. Average crystallite size of the particle's determined by the Sherrer formula using Match software found to be around ~ 400 nm for the synthesized bulk sample. The refinement results computed via FULLPROF software are in a very good agreement with the reference structural parameters [1].

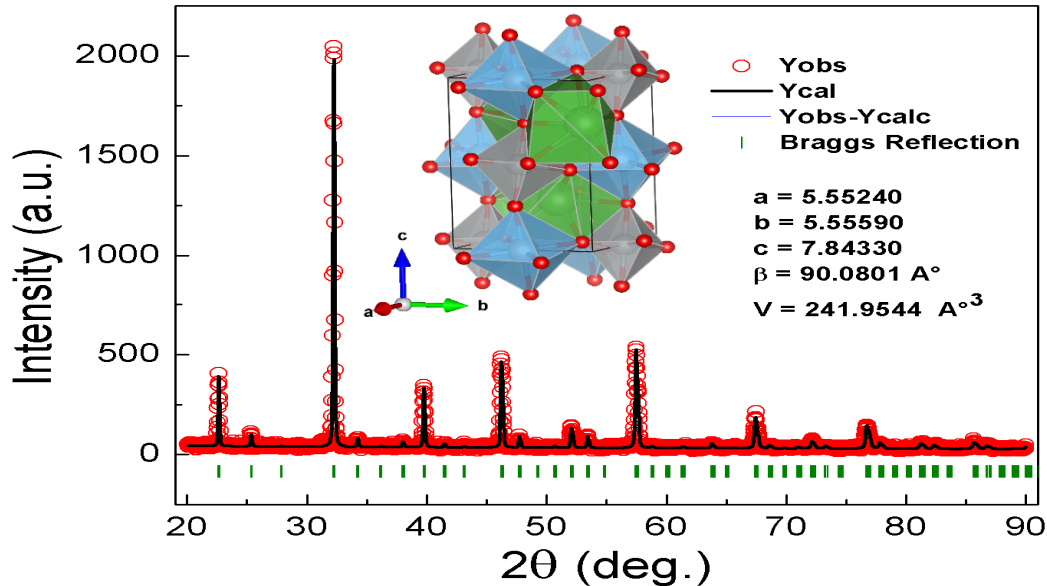


Figure 1. FULLPROF analysis of XRD patterns for LNTO compound. The right side figure shows the structure of $\text{La}_2\text{NiTiO}_6$ compound (Inset Image via VESTA software). (Obtained $\chi^2 = 1.09$ with Bragg R-factor: 6.77288 and RF-factor: 10.0819).

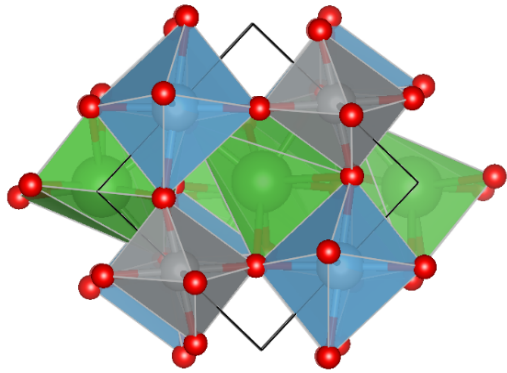


Figure 3a. Monoclinic structure with tilts of the octahedra.

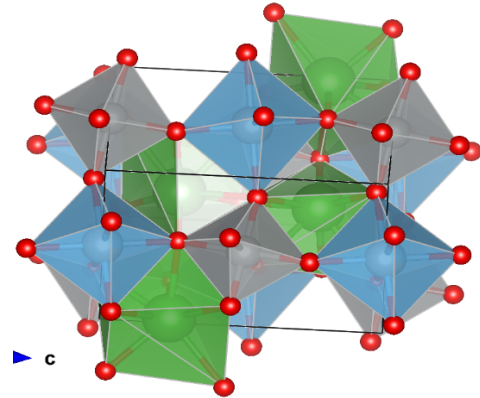


Figure 3b. Monoclinic structure with tilts of the octahedra.

The monoclinic structure with tilts of the octahedra is drawn in Figs. 3a. According to Glazer's notation, there is an $a^-b^+a^-$ configuration along the pseudo-cubic axes [1]. A positive superscript would denote the neighboring octahedra tilt in the same direction (in-phase) and a negative superscript implies in tilts of neighboring octahedra in opposite directions (out of phase). The view in Fig. 3a, 3b are along the pseudo-cubic a (or b) axis shows octahedra rotations with opposite sign. [Vesta crystal structure simulation software used to produce the images]. We draw a comparative view of the findings of our study in tabulated form; this is to compare the obtained parameters i.e. lattice constants, atomic site positions, bond length and bond angles, computed using the FULLPROF and VESTA software with the reference which have been used and fix to obtain a satisfactory symmetry for the synthesized $\text{La}_2\text{NiTiO}_6$ compound, with the SPuDS computed/predicted crystallographic data. Bold characters are used to distinguish the reference data from the other, a simple character set is used for the SPuDS data, while bold, italic and underlined font formation is used for the experimentally obtained data in all tables.

Table-I provides a comparative view over lattice parameters, Table-II summaries the comparison between the atomic positions, table-III (a) and Table-III (b) providing a comparative vision over the bond length and average bond distance respectively, while the Table-IV consists comparative bond angles.

Table-I: The refined lattice parameters and volume of the $\text{La}_2\text{NiTiO}_6$ compound derived from the sources mentioned in the text.

a/ Å	b/ Å	c/ Å	b/u	V/ Å ³
5102	5.6527	7.889	90.0095	241.721
5.5545(6)	5.5512(5)	7.8341(8)	90.08(2)	241.55(4)
<u>5.5524</u>	<u>5.5559</u>	<u>7.8433</u>	<u>90.0801</u>	<u>241.9544</u>

It can be seen that; Table-I and Table-II consists comparative lattice parameters and atomic positions values, it can be observe clearly that the experimentally obtained data values are much closer to the reference data and SPuDS software's predicted data. While Table (III-a) and Table (III-b) which consists the comparative data of the bond distances and average bond length between the A-O and B-O bonds, respectively. the overall length of the B-O bonds (Ti-O and Ni-O bond lengths) is closer to the value of 1.99 Å for the Ti-O bonds in $\text{La}_{2/3}\text{Li}_{0.11}\text{Ti}_2\text{O}_6$, where the mean B'-O bond lengths approach that of 2.04 Å found for Ni-O in other mixed oxides [1]. This is mainly due to the apical O atom connecting the TiO_2 and NiO_2 layers are found to move towards the Ti atom, so that the apical Ni-O bond length is ~ 2.01 Å and the Ti-O bond is ~ 1.91 Å, as expected if charge is transferred from Ti to Ni. Table (IV) which is to compare the bond angles, it's clear that the inter-octahedral Ni-O-Ti bond angles of $\text{La}_2\text{NiTiO}_6$ deviate strongly from 180°, indicating strong octahedral tilting as shown in Fig. 3a and 3b. This might be the case now, since The $\text{Ni-}e_g$ and $\text{Ti-}t_{2g}$ orbitals are orthogonal in the cubic double perovskite structure, but these

interactions become possible in the monoclinic double perovskite where the Ni-O-Ti bond angles are strongly reduced from 180° [1].

By comparing the crystallographic data (atomic positions and lattice parameter, bond lengths and bond angles) parameters obtained from the reference [1], SPuDS, VESTA and FULLPROF software for the synthesized $\text{La}_2\text{NiTiO}_6$ compound, it can be observe that the crystallographic parameters of the $\text{La}_2\text{NiTiO}_6$ compound obtained by using the FULLPROF and VESTA software, are in a satisfactory agreement with reference [1] and the SPuDS software's computed structure parameters as like the case of reference [4]. Apart the composition form of the synthesized compound must be $\text{La}_2^{3+}\text{Ni}^{2+}\text{Ti}^{4+}\text{O}_6^{2-}$. Though the difference in charge between Ni^{2+} and Ti^{4+} will be relatively small and the move towards an ordered structure is more likely to be determined by the size difference between the two cations (i.e., $r(\text{Ni}_{21}) \sim 0.69 \text{ \AA}$, $r(\text{Ti}_{41}) \sim 0.605 \text{ \AA}$). [1] The slight changes can be understand in terms of the effect of the experimental conditions and other depending related factors i.e. role of the binding media and surfactant, annealing temperature stoichiometry and etc.

Table-II: The atomic positions of the $\text{La}_2\text{NiTiO}_6$ compound derived from the mentioned sources.				
Atom	Site	x	y	z
La	4e	0.5132	0.541	0.292
	4e	0.5080(1)	0.5303(8)	0.2586(2)
	<i>4e</i>	<u><i>0.501</i></u>	<u><i>0.531</i></u>	<u><i>0.2558</i></u>
Ti	2d	$\frac{1}{2}$	0	0
	2d	$\frac{1}{2}$	0	0
	<i>2c</i>	$\frac{1}{2}$	<u><i>0</i></u>	<u><i>0</i></u>
Ni	2c	0	$\frac{1}{2}$	0
	2c	0	$\frac{1}{2}$	0
	<i>2d</i>	<u><i>0</i></u>	$\frac{1}{2}$	<u><i>0</i></u>
O1	4e	0.2173	0.2042	-0.0404
	4e	0.2286(2)	0.2173(3)	-0.0269(2)
	<i>4e</i>	<u><i>0.229</i></u>	<u><i>0.21</i></u>	<u><i>-0.046</i></u>
O2	4e	0.2982	0.719	-0.405
	4e	0.2945(2)	0.7106(2)	-0.0376(1)
	<i>4e</i>	<u><i>0.295</i></u>	<u><i>0.734</i></u>	<u><i>-0.02</i></u>
O3	4e	0.4191	-0.0121	0.2424
	4e	0.4266(2)	0.9928(1)	0.2411(1)
	<i>4e</i>	<u><i>0.42</i></u>	<u><i>0.992</i></u>	<u><i>0.225</i></u>

TABLE III (a): Selected bond lengths of the $\text{La}_2\text{NiTiO}_6$ compound derived from the sources as discussed in the text.					
Bond Length Comparison					
B-site	X-site	mult.	SPuDS	Reff.	<i>VESTA</i>
Ni (2C)	O (4e)	x 2	2.0813	2.034(1)	<u><i>2.21023</i></u>
Ni (2C)	O (4e)	x 2	2.0817	2.032(1)	<u><i>2.08808</i></u>
Ni (2C)	O (4e)	x 2	2.0815	2.071(1)	<u><i>2.12414</i></u>
Ti (2d)	O (4e)	x 2	1.9648	1.941(1)	<u><i>1.81344</i></u>
Ti (2d)	O (4e)	x 2	1.9652	1.990(1)	<u><i>1.90733</i></u>
Ti (2d)	O (4e)	x 2	1.9649	1.933(1)	<u><i>1.90523</i></u>

TABLE III (b): average bond length of the $\text{La}_2\text{NiTiO}_6$ compound derived from the sources as discussed in the text.			
La-O	2.81725	2.604	<u>2.576468</u>
Ni-O	2.0815	2.045	<u>2.140817</u>
Ti-O	1.964967	1.955	<u>1.875333</u>

TABLE IV: bond angles of the $\text{La}_2\text{NiTiO}_6$ compound derived from the mentioned sources.			
Ti-O1-Ni	154.58	161.4(2)	<u>154.7648(10)</u>
Ti-O2-Ni	154.46	155.3(1)	<u>158.8130 (3)</u>
Ti-O3-Ni	154.22	155.4(6)	<u>153.4150 (4)</u>

CONCLUSION

Conclusively, we may say that the polycrystalline $\text{La}_2\text{NiTiO}_6$ ceramics successfully prepared using sol-gel method. Monoclinic P21/n space group symmetry satisfactorily achieved without having any impurity phase. The crystal structure parameters acquired by the refinement of XRD data of LNTO using the FULLPROF software. The overall refined parameters are in a very good agreement with the reference structural parameters¹⁰. Apart the comparative study between the SPuDs predicted crystallographic data for the composition $\text{La}_2\text{NiTiO}_6$ so far is satisfactory and in a very good agreement with data obtained by the FULLPROF and VESTA software's.

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