

Crystal structure of LaVO_3 by Rietveld refinement method

R.T.A. Khan, J. Bashir, N. Iqbal, M. Nasir Khan*

Neutron Diffraction Group, NPD, PINSTECH, P.O. Nilore, Islamabad, Pakistan

Received 8 August 2003; accepted 21 October 2003

Abstract

Structure refinement of LaVO_3 was carried out using the whole pattern fitting or Rietveld method, which is a powerful technique for extracting structural information from powder diffraction data. The crystal structure refinement was done using powder X-ray diffraction data measured on a conventional diffractometer. The structure is orthorhombic, with space group $Pnma$ having lattice parameters $a = 5.5470(2) \text{ \AA}$; $b = 7.8401(5) \text{ \AA}$; $c = 5.5595(4) \text{ \AA}$, $V = 241.778(7) \text{ \AA}^3$, $Z = 4$, $D_x = 7.05 \text{ g cm}^{-3}$. The structure found is isostructural with GdFeO_3 in which all V sites are equivalent and VO_6 octahedra are regular. The results for the structural parameters are in a fairly good agreement with the synchrotron data published earlier.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; LaVO_3 ; Rietveld method

1. Introduction

The renewed interest in the compounds of the type ABO_3 especially the one belonging to transition metal oxide system such as LaVO_3 is because of their unusual electric and magnetic properties [1,2]. The interest stems with the discovery of high temperature superconductivity in cuprate compounds. LaVO_3 is known as a simple antiferromagnetic insulator [3] with $T_N \sim 150 \text{ K}$. Above this temperature, it is believed to possess distorted orthorhombic symmetry and below this temperature, it is considered monoclinic. This makes it a suitable parent material in studying the structural phase transition induced metal-insulator transition with proper doping. The system showed metal-insulator transition when doped with Ca for La [4], while it has been extensively studied with Sr doping for structural, magnetic and conduction investigations [5–7].

Different groups using different materials fabrication processes and measurements such as X-ray, neutron and synchrotron have studied the LaVO_3 system extensively over the past few decades for accurate determination of its crystal structure. The crystal structure determined so far remained at large controversial since its first emergence [8], where the structure was determined as cubic with

$a = 3.91 \text{ \AA}$. Later it was also found cubic with large lattice constant of $a = 7.842 \text{ \AA}$ in [9]. The system was also reported to possess tetragonal structure in Ref. [10]. From the Rietveld refinement of neutron powder diffraction data, the structure for this system was found to be cubic at room temperature with tetragonal distortion near Neel temperature [11]. Bordet et al. [12] reported the orthorhombic structure from their analysis of synchrotron X-ray and neutron diffraction data. They found that the distortion from the cubic symmetry is small but octahedral network distortion is comparable to other isostructural perovskites compounds. They attributed the controversy in the structure to data collection on the conventional X-ray diffractometer and emphasized their data of synchrotron and neutron diffraction. In order to resolve this controversy, we adopted a different approach for determining the crystal structure of LaVO_3 . The single-phase compound was first prepared by the usual solid-state reaction and diffraction data was collected using a conventional X-ray diffractometer. The structure was refined using full profile Rietveld analysis method [13] and the results are compared with those published earlier in the literature.

2. Experimental

Polycrystalline samples of LaVO_3 were prepared through the reduction of LaVO_4 in H_2 atmosphere for 6

* Corresponding author. Fax: +92-51-9290275.

E-mail address: nasir@pinstech.org.pk (M.N. Khan).

Table 1

Parameters calculated by *SPuDS* for the prediction of crystal structure of LaVO_3 system

Coordination geometry (tilt system symbol)	Tilt system number	Global instability index (GII)	Space group
$a^+a^+a^+$	#3	0.15569	$Im\bar{3}$ (204)
$a^+a^+c^-$	#5	0.07001	$P42/nmc$ (137)
$a^-b^+a^-$	#10	0.00275	$Pnma$ (62)
$a^-a^-a^-$	#14	0.00007	$R\bar{3}C$ (167)
$a^0b^+b^+$	#16	0.17004	$I4/mmm$ (139)
$a^0b^-c^+$	#17	0.08475	$CmCm$ (63)
$a^0b^-b^-$	#20	0.01864	$Imma$ (74)
$a^0a^0c^+$	#21	0.0699	$P4/mbm$ (127)
$a^0a^0c^-$	#22	0.0699	$I4/mcm$ (140)
$a^0a^0a^0$	#23	0.49587	$Pm\bar{3}m$ (221)

h at 900 °C. First, LaVO_4 was prepared through standard solid-state reaction by mixing appropriate amounts of 99.99% pure La_2O_3 and V_2O_5 . The mixture was first calcined at 1000 °C for 17 h followed by two-step approach 13 h of heating in air at 1200 °C with intermediate grinding between the two steps. Once the single phase LaVO_4 was obtained, it was annealed in air again at 1250 °C in order to further improve its crystallinity. LaVO_4 was then reduced in H_2 atmosphere to convert it to LaVO_3 . This approach is slightly different from some of the earlier works where V_2O_5 is reduced first and then reacted with La_2O_3 to form single phase LaVO_3 .

The powder diffraction pattern was collected at RINT 2000 Rigaku diffractometer in Bragg-Brentano geometry. $\text{Cu K}\alpha$ radiation monochromatized by a graphite monochromator was used to measure the diffraction pattern. The measurements were performed at room temperature in step scan mode over the angular range from 15° to 100° with a

step size of 0.02°. The data were refined using full-profile Rietveld analysis method.

3. Results and discussion

To resolve the controversy for the crystal structure, a different procedure was adopted. First the crystal structure was predicted using a software programme *SPuDS* [14]. The *SPuDS* has the ability to predict the crystal structure of perovskites, including those distorted by tilting of the octahedra. The user inputs the composition and oxidation state of each ion and the *SPuDS* calculate the optimal structure in ten different Glazer tilt system. This is performed by distorting the structure to minimize the global instability index (GII), while maintaining the rigid octahedral. The location of A site cation is chosen so as to maximize the symmetry of its coordination environment. An ideal perovskites structure has the ABO_3 stoichiometry and is composed of a three-dimensional framework of corner sharing BO_6 octahedra. The A site cation is surrounded by 12 anions in a dodecahedral environment due to coordinated cavities formed by the BO_3 network, and B cations are octahedrally coordinated by six anions. The octahedral tilting especially the central octahedral reduces the symmetry of the A site cation coordination environment and results in a change in the A–O bond lengths. However, there are multiple ways in which the octahedral can tilt, each leading to a different coordination environment for the A site cation. The Glazer notation describes the tilt system by rotation of BO_6 octahedral about the three orthogonal Cartesian axes, which are coincident with the axis of the cubic unit cell. The letters in the Glazer's notation [15] indicate the relative magnitude of the rotation about a given axis, such as the letters *a*, *b* and *c* imply the

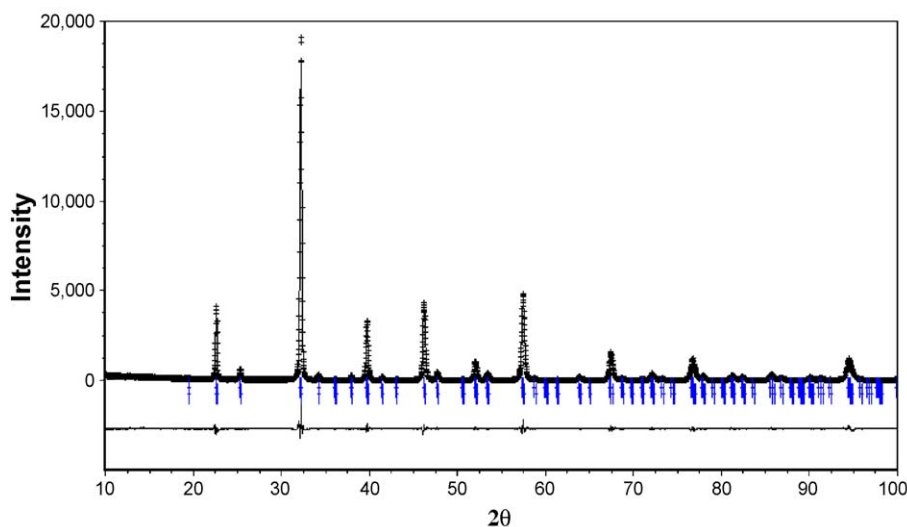


Fig. 1. The observed (.), and calculated (-), and difference powder X-ray diffraction profiles of LaVO_3 at room temperature. Reflection position is also marked.

unequal tilt about the x , y and z axes. A superscript either (+) or (−) are used to denote the phase of the tilt in the neighboring layer. Positive superscript denotes the tilt in the same plane (in-phase) while negative superscript implies the tilts of neighboring octahedral in opposite direction (out of phase). Superscript 0 denotes no tilt along that axis. The results obtained from this software showing the coordination geometry, tilt system, GII and respective space group for LaVO_3 system are summarized in Table 1. These results predict that experimental data can be best indexed in $R\bar{3}C$ space group where tilt is out of phase in all three axial directions and the GII value as predicted by *SPuDS* is lowest (0.00007) for this space group. Next comes the $Pnma$ space group where the tilt is equal but out of phase for a and c axes directions but in phase in the b axis direction and the GII is 0.00275.

The diffraction pattern was analysed by using the computer programme LHRIET-6 [16,17], which uses a full-profile Rietveld analysis method [13]. Based on the prediction of *SPuDS* results in Table 1, the diffraction pattern was

Table 2
Comparison of the refined parameters in the present work and those published by Bordet et al. for Synchrotron data

Atomic positions	Present results	Bordet et al. [12]
<i>La</i>		
x	0.0292(1)	0.0295(2)
y	0.25	0.25
z	0.9943(2)	0.9951(8)
B	0.42(1)	0.56(3)
N	1.00	1.00
<i>V</i>		
x	0.50	0.50
y	0.00	0.00
z	0.00	0.00
B	0.18(2)	0.45
N	1.00	1.00
<i>O₁</i>		
x	0.4897(8)	0.4880(6)
y	0.25	0.25
z	0.0764(19)	0.707(10)
B	0.93(8)	0.64(8)
N	1.00	1.00
<i>O₂</i>		
x	0.2801(13)	0.2831(6)
y	0.0338(9)	0.0387(4)
z	0.7155(12)	0.7168(6)
B	0.93(8)	0.62
N	2.00	2.00
a	5.5470(2)	5.5529(2)
b	7.8401(5)	7.8447(3)
c	5.5595(4)	5.5529(3)
γ	90	90
R_B	1.79	4.03
R_P	7.55	6.02
R_{WP}	10.61	7.73
R_E	6.74	6.83

Table 3

Bond lengths (Å) and bond angles (°) for LaVO_3 at room temperature			
$\text{V}-\text{O}_1$	$2.006(2) \times 2$	$\text{La}-\text{O}_1$	$3.027(5)$
$\text{V}-\text{O}_2$	$2.014(8) \times 2$	$\text{La}-\text{O}_1$	$2.594(5)$
$\text{V}-\text{O}_2$	$1.981(9) \times 2$	$\text{La}-\text{O}_1$	$3.180(10)$
		$\text{La}-\text{O}_1$	$2.396(10)$
		$\text{La}-\text{O}_2$	$2.685(6) \times 2$
$\text{O}_2-\text{V}-\text{O}_1$	88.87	$\text{La}-\text{O}_2$	$3.240(6) \times 2$
$\text{O}_2-\text{V}-\text{O}_1$	91.13	$\text{La}-\text{O}_2$	$2.753(7) \times 2$
$\text{O}_2-\text{V}-\text{O}_2$	91.02	$\text{La}-\text{O}_2$	$2.478(6) \times 2$
$\text{O}_2-\text{V}-\text{O}_2$	88.98		
$\text{V}-\text{O}_1-\text{V}$	155.30		
$\text{O}_1-\text{V}-\text{O}_2$	91.17		
$\text{O}_1-\text{V}-\text{O}_2$	88.83		
$\text{V}-\text{O}_2-\text{V}$	158.81		

first analysed by Rietveld method using space group $R\bar{3}C$, but the observed and calculated patterns did not fit well and some peaks were not even indexed in this space group. Therefore, we switched to the second space group $Pnma$ that has the second lowest GII value. The structural parameters predicted by *SPuDS* in this space group were taken as a starting point of the refinement. Initially only profile parameters were refined till the convergence was attained. After the minimum had been found for the profile parameters, these and all positional and isotropic thermal parameters were varied simultaneously. The occupancy factors for La, O_1 , and O_2 were also varied, but since they were close to full occupancies, during the final cycle, they were fixed at full occupancy. In total, 24 instrumental and structural

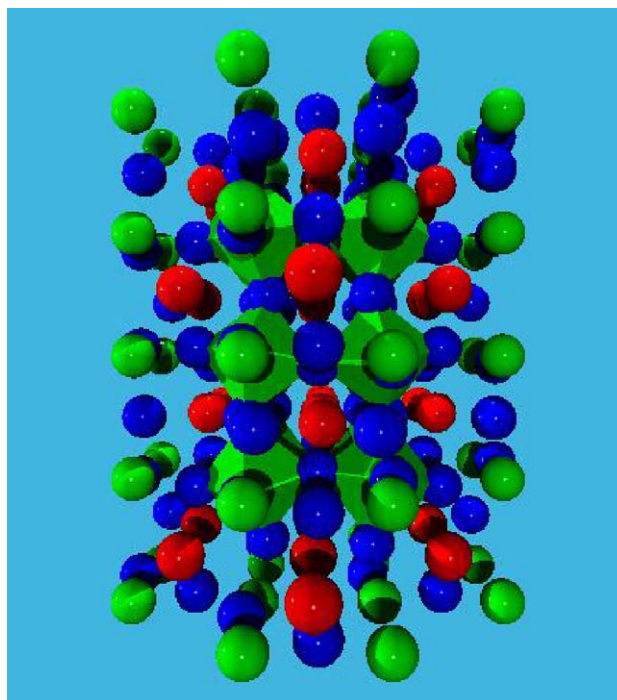


Fig. 2. Polyhedral presentation of LaVO_3 at room temperature viewed along the $[110]$ direction showing the octahedral tilting of LaVO_3 system. (Red is La, Green is V and Blue is oxygen).

parameters were refined simultaneously. The observed and calculated X-ray diffraction patterns are shown in Fig. 1. The Final values of the agreement factors were: $R_p = 7.55\%$; $R_{wp} = 10.61\%$; $R_{exp} = 6.74\%$ and $R_B = 1.79\%$, which are fairly good. As mentioned above, the earlier reports concerning the crystal structure of LaVO_3 was inconsistent; some suggesting a cubic perovskite transformed to tetragonal distorted perovskite structure, others quoted cubic to orthorhombic transition while some observed tetragonal structure at room temperature. The results of the Rietveld profile analysis of our room temperature XRD data exhibited the orthorhombic distortion of perovskites structure. The results obtained for the refined parameters are summarized and compared with the synchrotron data by Bordet et al. [12] in Table 2. The La cations are surrounded by 12 oxygen atoms arranged as a distorted cuboctahedron and the La–O distances vary between 2.478 and 3.24 Å as can be seen in Table 3. This means that all the 12 oxygen atoms cannot be viewed as first nearest neighbors because of this large distortion. We do consider the eight oxygen atoms with the shortest distance as first nearest neighbors and the remaining four oxygen atoms with larger distances as second nearest neighbors. Such behavior has already been reported on the basis of bond distances for the rare earth orthoferrite series in [18]. The V octahedral seems to be more stable and less distorted compared to La ones. The six oxygen's distances are comparable and only differ by less than one standard deviation as can be seen from Table 3. The 12 O–V–O angles vary in the range from 88.93° to 91.2° , which is comparable or even smaller than the one reported for synchrotron data by Bordet et al. [12]. As the perovskite arrangement in the ABO_3 structure comprises a three-dimensional network of corner sharing BO_6 octahedra, these octahedra tilt in such a way to create the proper coordination for the large cation. When the B cation is from transition metal group such as V in our case the 12-coordinated cuboctahedron is too large especially for large atoms even at room temperature and in order to make fit between $\text{A–O}/\sqrt{2}$ and B–O , the octahedra undergoes a tilting. As can be viewed from Fig. 2, which shows the octahedra tilting of LaVO_3 at room temperature along the $\{110\}$ direction. The octahedra seems to be rotated mainly along a and b axes and very slightly along the c -axis. The tilting usually does not induce any distortion of the octahedra, which on the contrary behave like a rigid entity. The distortion due to the tilting is completely absorbed by the

cuboctahedra, which are distorted, as the distances of 12 La–O vary over a large range.

4. Conclusion

In the present studies with a slight modification to the fabrication process of LaVO_3 combined with the XRD data from conventional diffractometer, we have made the single phase compound of LaVO_3 . The structural parameters from the Rietveld refinement of the XRD data showed that the structure of LaVO_3 is distorted orthorhombic; with space group $Pnma$ and is isostructural with GdFeO_3 . All V sites are crystallographically equivalent and the distortion lies in the 12 cuboctahedron mainly in the a and b axes. These results for the structural parameters obtained from the Rietveld analysis of the data are in a fairly good agreement to the results reported earlier for synchrotron data by Bordet et al.

References

- [1] A.V. Mahajan, D.C. Johnston, D.R. Torgeson, F. Borsa, Phys. Rev., B 46 (1992) 10973.
- [2] V.G. Zubkov, G.V. Bazuev, V.A. Perelyaev, G.P. Shveikin, Sov. Phys., Solid State 15 (1973) 1079.
- [3] J. Kikuchi, Y. Hiroshi, K. Yasuki, U. Yutaka, J. Phys. Soc. Jpn. 63 (1994) 3577.
- [4] C.N. Hoan, J.B. Goodenough, Phys. Rev., B 52 (1995) 324.
- [5] B. Reuter, M. Vollnik, Naturwissenschaften 50 (1963) 569.
- [6] R.G. Egddell, M.R. Harrison, M.D. Hill, L. Porte, G. Wall, J. Phys., Colloq. 17 (1984) 2889.
- [7] P. Dougier, P. Hagenmuller, J. Solid State Chem. 15 (1975) 158.
- [8] A. Wold, R. Ward, J. Am. Chem. Soc. 76 (1954) 1029.
- [9] H.L. Yakel, Acta Crystallogr. 8 (1955) 394.
- [10] T. Nakamura, G. Petzow, L.J. Gauckler, Mater. Res. Bull. 14 (1979) 649.
- [11] V.G. Zubkov, G.V. Bazuev, G.P. Shveikin, Sov. Phys., Solid State 18 (1976) 1165.
- [12] P. Bordet, C. Chaillout, M. Marezio, Q. Huang, A. Santoro, S.-W. Cheong, H. Takagi, C.S. Oglesby, B. Batlogg, J. Solid State Chem. 106 (1993) 253.
- [13] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
- [14] M.W. Lufaso, P.M. Woodward, Acta Crystallogr., B 57 (2001) 725.
- [15] A.M. Glazer, Acta Crystallogr., B 28 (1972) 3384.
- [16] C.J. Howard, R.J. Hill, AAEC Report No. M112, ANSTO, Lucas Heights Research Laboratories, NSW, Australia, 1986.
- [17] D.B. Wiles, R.A. Young, J. Appl. Crystallogr. 14 (1981) 149.
- [18] M. Marezio, J.P. Remeika, J.P. Dernier, Acta Crystallogr., B 41 (1985) 244.