Structural study of the α-phase of $Bi_4V_2O_{11}$

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In this work

$Bi_4V_2O_{11}$ can be considered as an intrinsically oxygen-deficient material that constitutes the first member of the Aurivillius family, characterized by alternating bismuth-oxygen layers and perovskite-like vanadium-oxygen blocks. The α polymorph is characterized by a highly ordered framework that incorporates regions of localized disorder within its vanadium–oxygen (V–O) layers. Several models have been proposed to describe the crystal structure of the α-phase of $Bi_4V_2O_{11}$, some derived from experimental data through Rietveld refinement and others based on theoretical approaches. Consequently, the precise structure of α-$Bi_4V_2O_{11}$ remains speculative. Such structural ambiguity is a common feature among Aurivillius phases, such as Bi_2WO_6 and δ-Bi_2MoO_6 which exhibit non-trivial structural complexities.
In this work, a series of models derived from an experimentally determined configuration was proposed [1]. The α-phase of $Bi_4V_2O_{11}$ was studied using density functional theory (DFT).

[1] Mairesse et al. (2003). Solid State Sciences, 5(6), 861-869

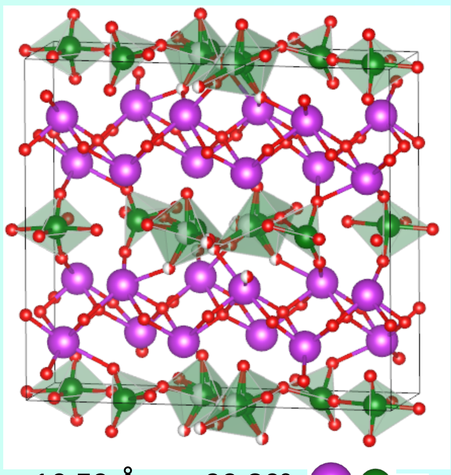
Methodology

A series of structural models derived from the experimentally determined configuration proposed by Mairesse et al. were constructed.
The α-phase is characterized by a disordered region within the vanadium–oxygen (V–O) layers, as evidenced by split and partially occupied vanadium and oxygen sites (occupancy of 0.5, indicated by ◑ in the figure). Several structural models were developed in order to eliminate the partial occupancies.

DFT calculations were performed with VASP code and considering the following parameters:

- Energy cut off: 400 eV
- K-point grid: 1 x 3 x 1
- Pseudopotencial: GGA/PBEsol
- Van der Waals forces correction: DFT-D3

Structure of Mairesee et al. [1]

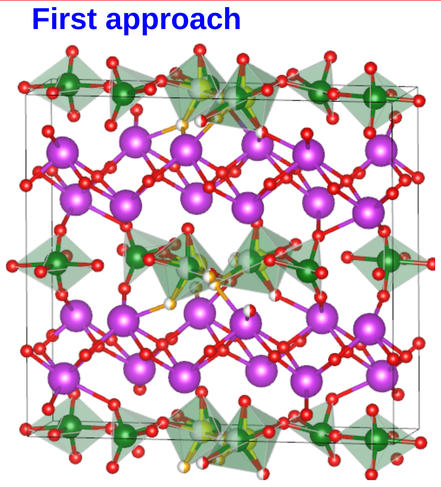


a=16.59 Å γ=90.26º
B= 5.61 Å
c=15.27 Å space group A2 Z=6

RESULTS

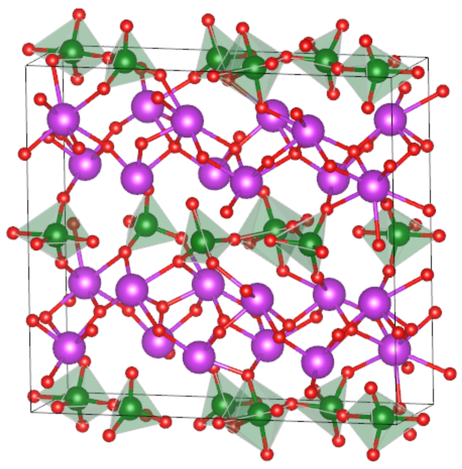
Structures

First approach



◑ Removed atoms

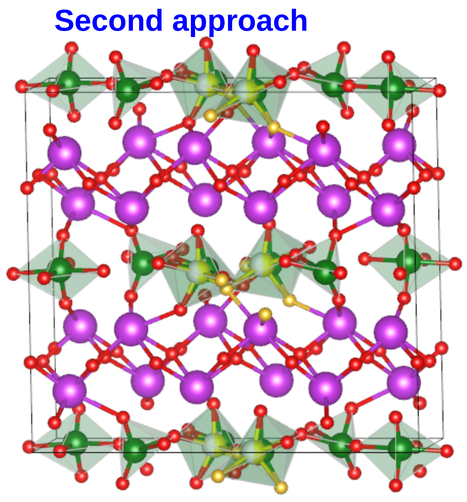
Relaxed structure



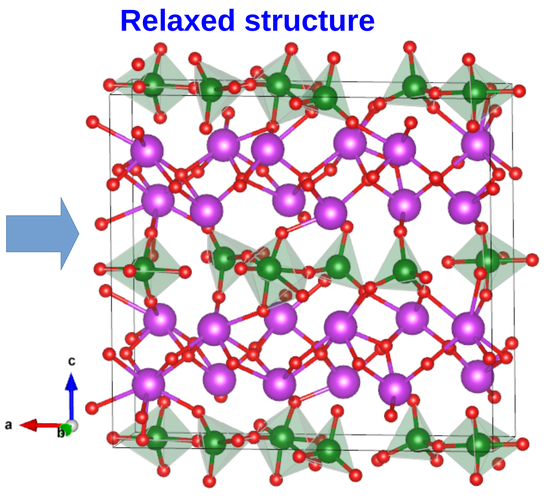
Configurational energies and lattice parameters

	Without cell relaxation	With cell relaxation
	a= 16.59 Å	a= 16.06 Å
	b= 5.61 Å	b= 5.43 Å
	c= 15.27 Å	c= 14.78 Å
	γ= 90.26º	γ= 90.3º
E(eV/FU)	125.76	125.80

Second approach

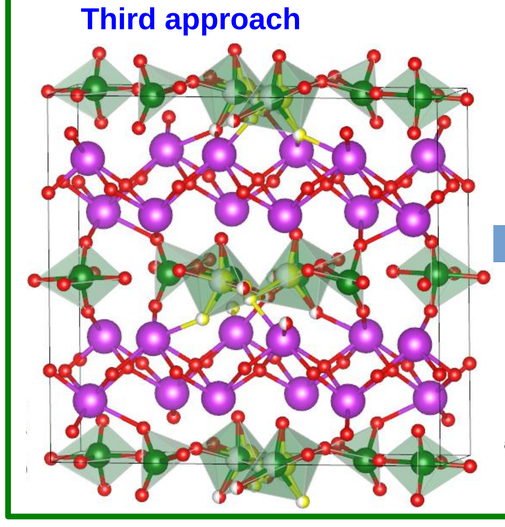


Relaxed structure

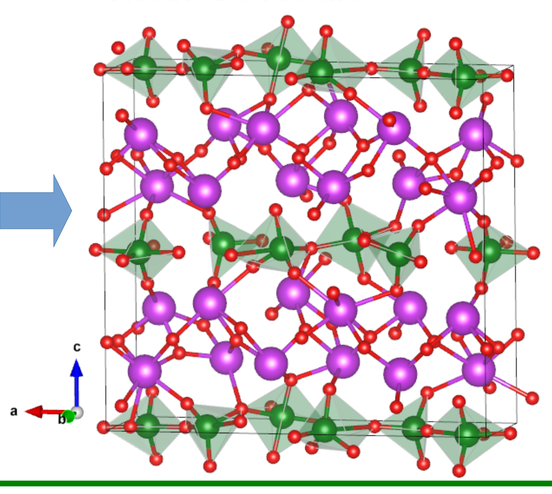


	Without cell relaxation	With cell relaxation
	a= 16.59 Å	a= 16.06 Å
	b= 5.61 Å	b= 5.43 Å
	c= 15.27 Å	c= 14.78 Å
	γ= 90.26º	γ= 90.3º
E(eV/FU)	125.76	-125.80

Third approach



Relaxed structure



	Without cell relaxation	With cell relaxation
	a= 16.59 A	a= 16.07
	b= 5.61 A	b= 5.437 A
	c= 15.27 A	c= 14.78 A
	γ= 90.26º	γ= 90.5º
E(eV/FU)	125.71	-125.84

Calculated and experimental X-ray diffraction patterns

Without cell relaxation

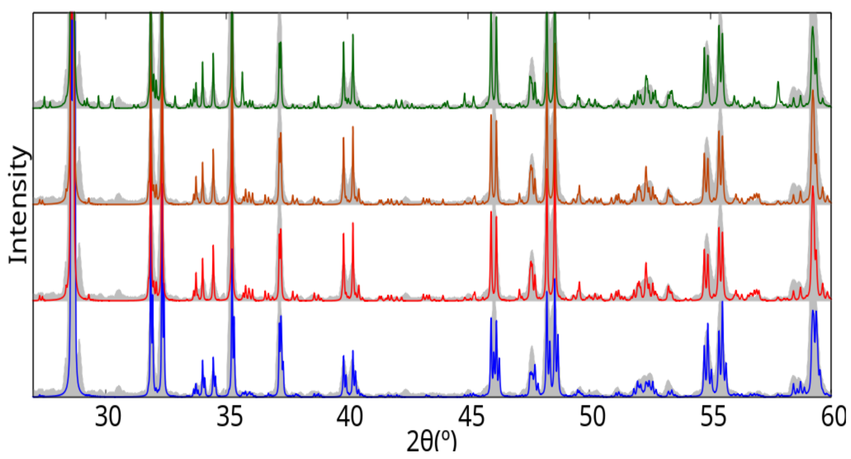


	Figure-of-Merit (FoM)
Experimental XRD	
Structure of Mairesee et al	0.8708
First approach	0.8456
Second approach	0.8457
Third approach	0.8502

With cell relaxation (lattice parameters were scaled +3.2%)
Comparison with other models

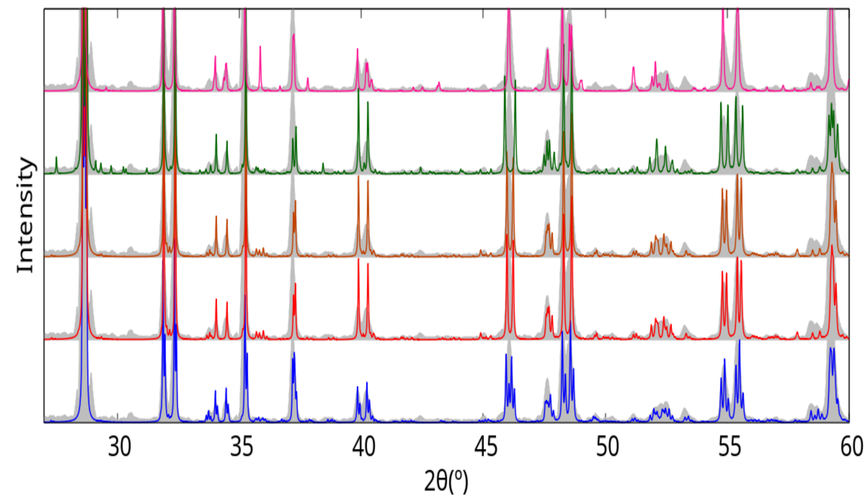


	Figure-of-Merit (FoM)	
Experimental XRD		
Structure of Mairesee et al	0.8708	
First approach	0.8561	**Good candidates**
Second approach	0.8561	
Third approach	0.8453	
Structure of MP-766025	0.8259	

CONCLUSIONS

A series of structures with comparable energy were identified, characterized by an equal number of oxygen vacancies per V–O layer, diverse vanadium and bismuth coordination environments, and significant variations in Bi–O and V–O bond distances.

The results from these models were analyzed and compared with literature data, focusing on the simulation of X-ray diffraction patterns to assess their correspondence. Two good candidates to describe α-phase of $Bi_4V_2O_{11}$ were obtained.

ACKNOWLEDGEMENTS

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