# **Inorganic Chemistry**

# On the Use of Dynamical Diffraction Theory To Refine Crystal Structure from Electron Diffraction Data: Application to $KLa_5O_5(VO_4)_2$ , a Material with Promising Luminescent Properties

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**S** Supporting Information

**ABSTRACT:** A new lanthanum oxide,  $KLa_5O_5(VO_4)_2$ , was synthesized using a flux growth technique that involved solid-state reaction under an air atmosphere at 900 °C. The crystal structure was solved and refined using an innovative approach recently established and based on three-dimensional (3D) electron diffraction data, using precession of the electron beam and then validated against Rietveld refinement and denisty functional theory (DFT) calculations. It crystallizes in a monoclinic unit cell with space group C2/m and has unit cell parameters of a = 20.2282(14) Å, b = 5.8639(4) Å, c = 12.6060(9) Å, and  $\beta = 117.64(1)^\circ$ . Its structure is built on Cresnel-like two-dimensional (2D) units ( $La_5O_5$ ) of 4\*3 ( $OLa_4$ ) tetrahedra, which run parallel to (001) plane, being surrounded by isolated  $VO_4$  tetrahedra. Four isolated vanadate groups create channels that host K<sup>+</sup> ions. Substitution led to a similar phase with a primitive monoclinic unit cell. A complementary selected area electron diffraction (SAED) study highlighted diffuse streaks associated with stacking faults observed on high-resolution electron microscopy



(HREM) images of the lithium compound. Finally, preliminary catalytic tests for ethanol oxidation are reported, as well as luminescence evidence. This paper also describes how solid-state chemists can take advantages of recent progresses in electron crystallography, assisted by DFT calculations and powder X-ray diffraction (PXRD) refinements, to propose new structural types with potential applications to the physicist community.

# 1. INTRODUCTION

One of the main motives in contemporary inorganic chemistry research is tailoring existing compounds to reach better and optimized properties, which is appears to provide promising results faster, with more certainty than looking for entirely new materials. However, the danger of this approach is a lack of interesting new structural architectures to be studied by chemists, physicists, or even industrial partners. A systematic research for new structural architectures is the only way to increase the number of compounds available in the databases and potentially investigated for their properties, and, as such, should receive special attention in fundamental research.

In this context, materials based on oxo-centered units have been thoroughly studied over the last decades,<sup>1</sup> leading to a wide panel of interesting architectures and topologies. Plethora of bismuth-based compounds with various dimensionalities were intensively isolated and characterized. Their cationic backbone is built on an association of  $O(Bi,M)_n$  (M = transition metal or alkali metal and  $n = 1, ..., \infty$ ) tetrahedra sharing edges or corners to form one-dimensional (1D) ribbons or columns, two-dimensional (2D) layers, or three-dimensional (3D) networks associated with XO<sub>4</sub> (X = P, As, V, Mo, Cr, ...) polyanions or halogens in most cases. Some of these phases present many potentially interesting physical properties, such as oxygen ion conductivity,<sup>2</sup> ferroelectricity,<sup>3,4</sup> catalytic properties,<sup>5–7</sup> or superconductivity.<sup>8</sup> In order to modify architectures and vary properties, bismuth(III) may be substituted by other cations. Particularly, the  $La^{3+}$  cation is well-known to be able to adopt the same configuration of oxo-centered tetrahedra OLa,<sup>1</sup> as often encountered in many bismuth compounds. Indeed, Bi<sup>3+</sup> and La<sup>3+</sup> have almost identical ionic radii (1.03 Å), but the La<sup>3+</sup> cation does not exhibit the pronounced stereoactivity of bismuth, because of the absence of the *p*-hybridized  $6s^2$  lone electron pair. To date, only a few architectures have been obtained that could adopt alternatively bismuth or lanthanum in the cationic backbone. This paper mainly focuses on our attempts to synthesize the La homologue of  $BiCu_2O_2(VO_4)$ , i.e.,  $LaCu_2O_2(VO_4)$ .<sup>9,10</sup> For that, because of the well-known refractory behavior of lanthanum oxides, in a first step,  $La(OH)_3$ , CuO, and  $V_2O_5$  were mixed together and heated to 1200 °C. Unfortunately, this "brutal" approach systematically

Received: November 17, 2015

led to lanthanum orthovanadate (LaVO<sub>4</sub><sup>11</sup>) and copper(II) oxide. To overcome this problem, an alternative flux growth technique was attempted, to modify the result, and KCl was tested as flux, as proposed in ref 12, leading, by serendipity, to the title compound and also a broad series of new phases. The new structural type was solved by a combination of electron diffraction, density functional theory (DFT) calculations, and powder X-ray Rietveld refinement. In addition, to improve the accuracy of the electron data refinement, instead of using the kinematical approximation (only valid for X-ray, but not for electron diffraction), we applied the newly developed method of dynamical refinement from electron diffraction tomography data that takes into account multiple scattering. To our knowledge, this is the first application of this innovative approach in the analysis of an unknown compound. Finally, to reveal potential functions to this new compound, first physical characterizations were undertaken, on the basis of expected properties, i.e., oxidation catalytic and luminescence properties. because of distorted VO4 groups. The luminescence is induced by these vanadate groups, because it has no electron in the 4f orbitals for the La<sup>3+</sup> cation.

# 2. EXPERIMENTAL SECTION

**2.1. Synthesis.** For the synthesis of polycrystalline  $ALa_5O_5(VO_4)_2$ , a stoichiometric amount of  $La(OH)_3$ ,  $V_2O_5$ , and  $A_2CO_3$  (where A = Li, Na, and Rb) was ground in an agate mortar, placed in an alumina crucible, preliminary heated at 600 °C for 12 h, and then heated at 1000 °C for 48 h. The furnace was then switched off. To date, our attempts to obtain single crystals of the corresponding powder systematically failed, probably because of the refractory character of lanthanum.

2.2. Electron Microscopy and Structure Refinement. Transmission electron microscopy (TEM) studies and energy-dispersive Xray spectroscopy (EDX) analysis were performed on a FEI Tecnai G2 20 microscope. Electron diffraction (ED) patterns were obtained with a precession system (Nanomegas Spinningstar). The material was crushed and dispersed on a holey carbon film that was deposited on a copper grid. The 3D electron diffraction tomography data were collected in steps of 1°, 111 nonoriented PED patterns were collected (at tilt angles from  $-60^{\circ}$  to  $+50^{\circ}$ ), with a precession angle of  $1.2^{\circ}$ , which is not too high to minimize the superposition of spots, but is large enough to reduce dynamical effects. The series of diffraction images was processed using the computer program PETS.<sup>18</sup> The indexing and integration procedure is analogous to commonly used procedures in X-ray diffraction (XRD). Its particular implementation in PETS is described in ref 41. The structure was solved using the program Superflip<sup>20</sup> and refined in Jana2006,<sup>19</sup> first in the kinematical approximation and then also using the dynamical refinement method.<sup>21–23</sup> The computer-simulated HREM images were calculated using the JEMS program.4

**2.3. Powder X-ray Diffraction.** Powder X-ray diffraction (PXRD) data were collected at room temperature (RT) using a Bruker AXS D8 Avance diffractometer (Bragg–Brentano geometry) that was equipped with a 1D PSD detector (Lynx-Eye); Cu K $\alpha_{1,2}$  radiations were used in the range of  $2\theta = 5^{\circ}-120^{\circ}$ , with a  $0.02^{\circ}$  step and a counting time adjusted to obtain a good statistical count. The JANA 2006 program<sup>19</sup> was used for Rietveld refinement, using a Pseudo-Voigt function for the peak profiles; the atomic positions, as well as the isotropic atomic displacements of all atoms, were refined.

**2.4. Computational Methods.** Electronic structure calculations were carried out within the DFT formalism, using the Vienna Ab Initio Simulation Package (VASP).<sup>43</sup> The calculations were carried out within the generalized gradient approximation (GGA) for the electron exchange and correlation corrections, using the Perdew–Wang<sup>44</sup> functional. Projector augmented-wave (PAW)<sup>45</sup> pseudo-potentials were employed. Structural relaxation of both atomic positions and unit-cell parameters was carried out using a plane wave energy cutoff

of 550 eV and 30 k-points in the Irreducible Brillouin Zone (IBZ). The convergence was reached with residual Hellman–Feynman forces on the atoms smaller than 0.03 eV Å<sup>-1</sup>.

**2.5. Catalytic Test.** Reaction of ethanol oxidation was performed using a fixed-bed reactor. Before the experiment, 200 mg of sample was mixed with 200 mg of SiC in order to homogenize the temperature inside the catalytic bed. Catalytic test was carried out in a glass reactor consisting of a 10-mm-diameter tube connected online with a gas chromatography—mass spectroscopy (GC-MS) apparatus, which performed an analysis every 3 min. The reactor was located in an oven that was controlled by two thermocouples, allowing a precise temperature of the catalytic bed. Reaction was performed in a range of temperature comprise between 250 °C and 375 °C at constant atmospheric pressure. The total gas flow rate was not changed (gas hourly space velocity (GHSV) of 2256 h<sup>-1</sup>) during reaction, and the composition was maintained at 13.2% ethanol, 6% oxygen, and 40.8% helium (as a carrier gas). The conversion of ethanol for each product is defined as

ethanol conversion of X (%) = 
$$\frac{(n^0 - n) \times 100}{n^0}$$

where  $n^0$  is the initial number of moles of ethanol and n is the number of moles of ethanol after the analysis has been performed, and the selectivity for each product (S) is presented and defined as

$$S(\%) = \frac{n_{\rm CX} \times n_x}{n_{\rm CEth}(n^0 - n)}$$

where  $n_{\text{CX}}$  is the number of carbons in the product X,  $n_{\text{X}}$  the number of moles of product after the analysis has been performed, and  $n_{\text{CEth}}$  the number of carbons in ethanol (i.e.,  $n_{\text{CEth}} = 2$ ).

**2.6. Luminescence.** The excitation and emission spectra were performed on a SAFAS-Monaco Xenius spectrofluorometer that was equipped with a xenon lamp as an excitation source. All measurements were conducted at room temperature.

# 3. RESULTS AND DISCUSSION

3.1. Preliminary Study. As already stated, the precursors mentioned above were ground in an agate mortar, then placed in an alumina crucible in order to undergo a heat treatment at 600 °C for 12 h and then 1200 °C for 48 h and systematically led to a mixture of LaVO<sub>4</sub> and CuO. This first attempt was unsuccessful, but KCl was then added to decrease the temperature of the reaction and increase the reactivity. After washing with hot water, the resulting powder of a sample of nominal composition (La<sub>4</sub>O<sub>4</sub>)Cu<sub>2</sub>(VO<sub>4</sub>)<sub>2</sub>, melted in KCl, was investigated using PXRD. The pattern obtained evidenced two crystallized phases: the first one, a minor phase, is consistent with the presence of  $LaVO_4$ ,<sup>11</sup> while the second one, which is predominant, was not found in the ICDD database (within a tolerance of 1.5 Å for unit-cell parameters). It was indexed afterward with DICVOL<sup>13</sup> in a C-centered monoclinic unit cell with parameters a = 20.29 Å, b = 5.96 Å, c = 12.59 Å, and  $\beta =$ 117.89°. EDXstudy confirmed the presence of LaVO<sub>4</sub> and a second phase, showing, besides lanthanum and vanadium, the unexpected presence of potassium instead of the expected copper, in an average composition of K:La:V = 7:40:9 (average of 10 different crystals). Attempts to solve the structure *ab initio* with powder X-ray data were not successful, and, because our attempts to get single crystals systematically failed, we decided to find the structure model using precession-assisted electron diffraction tomography.

**3.2. Crystal Structure Determination by Transmission Electron Microscopy.** The procedure detailed in ref 14 has been applied in this study.

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3.2.1. Preliminary Study from Oriented Patterns. In the first step, a "classical" SAED study was conducted on a crystallite containing lanthanum, potassium, and vanadium. The reconstitution of the reciprocal space led to a monoclinic cell with approximate lattice parameters of a = 20.2 Å, b = 5.9 Å, c = 12.6 Å, and  $\beta = 118^{\circ}$ . The comparison between the Zero Order Laue Zone (ZOLZ) and the First Order Laue Zone (FOLZ) allows one to determine the extinction symbol, according to the tables given in ref 15. The examination of the difference of periodicity and shift between the ZOLZ and FOLZ of the [010] zone axis pattern (ZAP) leads to the extinction symbol C- (see Figure 1).



**Figure 1.**  $KLa_5O_5(VO_4)_2$ : [010]-oriented zone axis pattern (ZAP). The comparison between the Zero Order Laue Zone (ZOLZ) and Higher Order Laue Zone (HOLZ) leads to a C- extinction symbol, because no difference of periodicity is observed but a shift is detected. The labels -1, 1, and 0 refer to the order of the Laue Zone.

3.2.2. Structure Model by Precession Electron Diffraction Tomography-Kinematical Refinement. A precession electron diffraction tomography (PEDT) dataset was collected on the nanocrystal based on the approach proposed by Kolb et al.<sup>16,17</sup> 111 nonoriented PED patterns were collected (every 1° from a tilt range of  $-60^{\circ}$  to  $+50^{\circ}$ ) on a TEM FEI Tecnai, operating at 200 kV ( $\lambda$  = 0.0251 Å) with a precession angle of 1.2°. This series of diffraction images was processed using the PETS software.<sup>18</sup> After peak hunting and microscope parameters refinement (i.e., the adjustment of the angle between the projection of the tilt axis on the pattern and the horizontal axis, angle depending on the camera length and on the exact focusing conditions), the 3D positions of diffraction spots were indexed in Jana 2006,<sup>19</sup> leading to the following cell parameters: a = 20.293 Å, b = 5.958 Å, c = 12.680 Å,  $\alpha =$ 90.12°,  $\beta = 118.11^\circ$ , and  $\gamma = 90.15^\circ$ . After the indexing, the reflection intensities were integrated by PETS, resulting in a list of 3782 pseudo-kinematical reflection intensities. These

intensities were imported in Jana 2006. Analysis of intensities suggested the following space groups: C2/m, C2, or Cm. The structure was solved by the program Superflip,<sup>20</sup> which confirmed the space group C2/m. The structure was then refined by Jana2006.

Despite the use of PED (which is known to reduce the dynamical effects due to multiple diffraction) and the use of "nonoriented" patterns (which are also less affected by multiple diffraction and, thus, are more kinematical), the data are still affected by dynamical diffraction effects, and the deviation from the kinematical approximation results in relatively large refinement (R) values and limited accuracy of the refined model. Nevertheless, the derived structural model is coherent from chemical point of view and it provided also the chemical composition of the compound. The formula deduced from the kinematical PEDT model was KLa<sub>5</sub>V<sub>2</sub>O<sub>13</sub>, in good agreement with the previous EDXanalysis. With this composition, a pure powder was obtained without any trace of LaVO<sub>4</sub> impurity. All data were recollected on the pure sample.

3.2.3. Accurate Structure Model by Dynamical Refinement of PEDT Data. To improve the accuracy of the structure model, we employed a recently developed method of dynamical refinement. This method, which was described in a series of publications,<sup>21–23</sup> uses (P)EDT data for the least-squares refinement in a similar way as described in the previous section, but the theory used to calculate the model intensities is not the kinematical diffraction theory but the full dynamical diffraction theory. As a result, the figures of merit are much lower and the structure models are more accurate, compared to the kinematical refinement. In ref 23, it was shown that the typical average error in atomic positions obtained with this method is <0.02 Å, and occupancies of partially occupied sites can also be reliably refined.

The refinement proceeded along the guidelines presented in ref 23. Recommended settings were used for all parameters. The refinement of anisotropic displacement parameters led to a few nonpositive definite displacement tensors, and the displacement parameters were therefore refined as isotropic. No other constraints or restraints were employed in the refinement. The refinement resulted and details of the refinement are summarized in Table 1.

**3.3. Rietveld Analysis and DFT Optimizations.** Powder X-ray data for the title compound were collected under experimental conditions given in Table 1. For all atoms, the initial atomic positions have been taken from the structural model obtained from kinematic PEDT data. The refinement rapidly converged without any particular problem, with acceptable values of isotropic atomic displacement parameters. The experimental and calculated patterns are shown in Figure 2.

To validate the different structure models, we decided to optimize the structures using DFT calculations starting from both the kinematical and dynamical models (see Table 2, as well as Table S3 in the Supporting Information). DFT serves to pinpoint the clearly wrong aspects of the structure, while certain small differences are possible and expected. For the kinematical model, the full optimization provided unit-cell parameters in very good agreement with the experiment, with discrepancies of <2%. However, some noticeable changes occurred within the structure, in particular, a significant shift of the O9 position with local relaxation around this atom. The comparison between the dynamically refined model with the DFT optimization shows only one important discrepancy: the

#### Table 1. Refinement Details for $KLa_5O_5(VO_4)_2$

parameter	value				
General Data					
space group	C2/m (No. 12)				
cell parameters					
a	20.2093(11) Å				
Ь	5.8710(1) Å				
с	12.5869(1) Å				
β	117.71(1)°				
V	1322.11(1) Å <sup>3</sup>				
Statistical Parameters for Rietveld Refinement					
No. of reflections	1099				
No. of refined parameters	57				
N-P+C	5561				
R <sub>P</sub>	3.47				
$\omega R_{\rm p}$	4.96				
goodness of fit, GOF	2.96				
$R_{\rm all}$	4.64				
R <sub>obs</sub>	4.58				
$\omega R_{\rm obs}$	5.91				
G <sub>1</sub> (texture)	0.0651(26)				
G <sub>2</sub> (texture)	0.070(1)				
Statistical Parameters for Dynamical Refinement from EDT Data					
No. of reflections	8355				
No. of refined parameters	171				
No. of diffraction patterns	114				
data completeness	72.5%				
R <sub>obs</sub>	10.06				
R <sub>all</sub>	14.33				
goodness of fit, GOF	2.85				

V2–O6 distance, which refines to 1.58 Å and is estimated by DFT as 1.73 Å (see Table S1 in the Supporting Information). The distance of 1.58 Å appears to be too short for a V–O distance in a VO<sub>4</sub> tetrahedron.<sup>24</sup> To obtain the final refined model, we have therefore repeated the dynamical refinement

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Table 2. Unit-Cell Parameters Comparison between	
Kinematical, Optimized Kinematical, Dynamical, Optimized	ed
Dynamical, and Rietveld Refinements	

ref	a (Å)	b (Å)	c (Å)	$\beta$ (deg)
kin	20.2282	5.8639	12.6060	117.64
OPT kin	20.3099	5.9589	12.6649	118.212
dyn	20.2962	5.9249	12.5966	117.5825
OPT dyn	20.3051	5.9605	12.6623	118.243
Riet	20.2093	5.8710	12.5869	117.71

with a soft restraint on the V–O6 distance set to 1.70(1) Å. We consider this model to be the best structure model of  $KLa_sO_s(VO_4)_2$ .

The results show that the dynamical model compares much better to the DFT-optimized one than the kinematical refinement, with lower divergence for both unit-cell parameters and atomic positions, and with only one slightly anomal distance (see Table 3, as well as Table S1 in the Supporting Information). As a further validation procedure, HREM image simulations were calculated on the basis of this model, and compared to the experimental ones. For a defocus of -35 nm and a thickness of 35 Å, the simulated [010] image matches perfectly with the experimental one (Figure 3). For these conditions, the cations appear as black dots and the tunnel is highlighted as white squares. The crystal-structure data for KLa<sub>5</sub>O<sub>5</sub>(VO<sub>4</sub>)<sub>2</sub> phase was deposited at the Cambridge Structure Depository (No. CSD-430461).

**3.4. Crystal Structure Description.** The structure may be described using the antiphase approach, meaning an association of polyhedra centered on anions and surrounded by cations. Here, the aforementioned polyhedra are  $OLa_4$  tetrahedra, sharing edges to build 2D Cresnel-like layers condensed in a stepwise manner with weight and steps equal to 3 and 4 tetrahedra, respectively (Figure 4). These layers are surrounded by isolated  $VO_4$  groups organized together, in groups of four, to build the so-called "tunnels" already observed in related



**Figure 2.** Final observed (red), calculated (black), and difference plots (blue) obtained for the powder X-ray diffraction (PXRD) Rietveld refinement of  $KLa_5O_5(VO_4)_2$ .

Table 3. Atomic Positions Deviations between Kinematical/ Dynamical Refinement and Respective DFT Optimizations and between the Two Optimizations

atom– atom	kinematical opt./ dynamical opt. deviation	kinematical/ kinematical opt. deviation	dynamical/ dynamical opt. deviation	dynamical + restraint/ dynamical opt.
K1-K1	0.00119	0.02287	0.00473	0.00309
La1-La1	0.00000	0.04221	0.01714	0.01754
La2—La2	0.00127	0.07360	0.01296	0.01432
La3–La3	0.00609	0.07131	0.05472	0.05504
La4-La4	0.00363	0.05312	0.03779	0.03776
La5–La5	0.00238	0.18872	0.07809	0.07834
V1-V1	0.00404	0.19617	0.02925	0.02840
V2-V2	0.00758	0.00878	0.01965	0.02110
01-01	0.00140	0.11631	0.05265	0.05223
02–02	0.00494	0.12391	0.02425	0.02505
03-03	0.01478	0.16954	0.10999	0.10323
04-04	0.00808	0.12019	0.02839	0.03274
05-05	0.01077	0.15440	0.01691	0.01937
06-06	0.01136	0.15085	0.18484	0.10040
07-07	0.00874	0.33877	0.05518	0.05275
08-08	0.00000	0.08969	0.05682	0.06269
09–09	0.00238	0.34128	0.02610	0.02764
average	0.00591	0.13304	0.04762	0.04304
maximum	0.01478	0.34128	0.18484	0.10323



**Figure 3.** (a) High-resolution image corresponding to the diffraction pattern of Figure 1. The comparison with a simulated image, shown as panel (b), obtained for a defocus of 35 nm and a thickness of 3.5 nm allows the superimposition of the projected structure. For these conditions, the cations appear as black dots and the white squares highlight the vanadate groups.

bismuth-based materials. These tunnels are formed by four XO<sub>4</sub> groups, running parallel to the *b*-axis (~5.5 Å, corresponding to the height of two O(La,Bi)<sub>4</sub> tetrahedra). These cationic channels are hosting here K<sup>+</sup> cations. The residual electronic density remains quite high around  $1/_2$ , *y*,  $1/_2$ , which is quite usual in such tunnel structures.<sup>25</sup> Indeed, it is noteworthy that several cations (two in maximum) may occur in the tunnels.<sup>26</sup> Here, the occupancy rate of K was arbitrary fixed to 1, resulting in one cation per one tunnel and one unit cell.



**Figure 4.**  $KLa_5O_5(VO_4)_2$  crystal structure showing the 4\*3 *Td* Cresnel-type 2D units of  $(OLa_4)$  tetrahedra (the " $\otimes$ " symbol denotes the infinite character of the ribbons perpendicular to the plane of the figure).

The stabilization of oxo-centered inorganic structure with Cresnel-like geometry is rarely observed in the literature, and the final dimensionality of the blocks is closely related to the nature of the main supporting cation. In the case of lead-based materials, polycationic blocks are only chains built on edgeshared OPb<sub>4</sub> tetrahedra, leading to chains of variable width:  $2Td^*2Td$  in  $Pb_2SiO_4^{27}$  (Figure 5a)),  $3Td^*2Td$  in  $Pb_5O_4(MoO_4)^{28}$  (Figure 5b)), or  $7Td^*4Td$  in  $[Pb_{10}O_7]$ - $(OH)_2F_2(SO_4)^{29}$  (Figure 5c)). Concerning lanthanide- and bismuth-based materials, Cresnel-like geometry is usually associated with the presence of 2D layers. For example, in  $Nd_4O_4(GeO_4)^{30}$  (Figure 5d)),  $[Nd_4O_4]$  layers exhibit a ladderlike topology with the width and height of steps being equal to 3Td\*3Td. Landa-Canovas et al. recently reported a family of bismuth oxides with the general formula  $Bi_{2n}Mo_{n-2}O_{6n-6}$  (n = 5-8) (the case of n = 5 is shown in Figure 5e)).<sup>31</sup> In this series, ribbons of variable width equal to noverlap by terminal edge sharing to create a zigzag layer. Another compound,  $Bi_{18.71}Cr_{0.27}P_6O_{43.22}^{32}$  (Figure 5f)) is built on n = 8 ribbons sharing edges with perpendicular n = 3 ribbon connections. It is noteworthy that, in case of zigzag layers, the general stability of the edifice is ensured by additional O atoms filling empty space at the angles of the zigzag layers through OBi3 triangular edifices. In the case of our compound, the global stability of the structure is ensured by similar additional OLa<sub>3</sub> units (Figure 4). Finally, the condensation of  $OM_4$  (M = Pb, Bi, Ln) leads to units of variable sizes, related to the dimensionality of the parent structure: PbO being 2D leads to 1D chains, whereas La2O3 and Bi2O3 are 3D and give 2D Cresnel-like layers.

**3.5. Alkali-Metal Substitution.** With the objective of measuring the impact of the ionic radius of the alkali metal on



**Figure 5.** Various width and height of Cresnel-like layers of various compounds: (a)  $2Td^*2Td$  in Pb<sub>2</sub>SiO<sub>4</sub>, (b)  $3Td^*2Td$  in Pb<sub>5</sub>O<sub>4</sub>(MoO<sub>4</sub>), (c)  $7Td^*4Td$  in Pb<sub>10</sub>O<sub>7</sub>(OH)<sub>2</sub>F<sub>2</sub>(SO<sub>4</sub>), (d)  $3Td^*3Td$  in Nd<sub>4</sub>O<sub>4</sub>(GeO<sub>4</sub>), (e)  $2Td^*5Td$  in Bi<sub>2</sub>Mo<sub>8</sub>O<sub>24</sub>, and (f)  $3Td^*8Td$  in Bi<sub>1871</sub>Cr<sub>027</sub>P<sub>6</sub>O<sub>43.22</sub>.



Figure 6. Powder X-ray patterns of Li, Na, K, and Rb compounds. As shown in the insert, the unit-cell volume is a function of the ionic radii of alkaline apart for  $Li^+$  cation. In this case, the Bravais lattice is different, P-centered instead of C-centered, and shown by (hkl) index enhancement.

Table 4. Unit-Cell Parameters of ALa<sub>5</sub>O<sub>5</sub>(VO<sub>4</sub>)<sub>2</sub> Powders Calculated Using Jana 2006 Software

Α	a (Å)	b (Å)	c (Å)	$\beta$ (deg)	V (Å <sup>3</sup> )
Li	22.691(2)	5.905(1)	11.828(1)	120.068(5)	1371.48(19)
Na	19.949(2)	5.912(1)	12.460(1)	117.463(3)	1303.87(14)
K	20.228(2)	5.864(4)	12.606(1)	117.636(3)	1324.68(22)
Rb	20.326(2)	5.845(1)	12.660(1)	117.690(3)	1331.72(16)

the crystal structure, the substitution of K by Li, Na, Rb, and Cs was tested. Powder syntheses were performed using the procedure detailed in Experimental Section. Na and Rb substitution resulted in compounds giving similar XRD patterns to the title compound, with only small displacements of peak positions related to the modification of unit-cell parameters, probably due to variations of the atomic size of the alkaline component (see Figure 6 and Table 4). However, the substitution of lithium induced a rather strong modification of the powder X-ray pattern. Therefore, the lithium-based compound was studied in detail by electron diffraction, both in diffraction and high-resolution image modes. The former study evidenced the same kind of monoclinic unit cell, slightly distorted (Table 4), but with a primitive Bravais lattice, instead of being C-centered. This violation of C centering is due to the presence of additional spots evidenced by white arrows on [010] ZAP (Figure 7). The observation of this ZAP shows



**Figure 7.** [010] zone axis: HREM images showing shear planes (green arrows) in case of the lithium sample and the corresponding electron diffraction pattern, showing diffuse streaks. The white arrows indicate the weak spots responsible of the P Bravais lattice. The size of intergrowth is variable, with several examples evidenced here.

diffuse streaks, in accordance with the HREM study, which proved the presence of defects observed on Figure 7. Many crystallographic shear planes with a small shift along the *c*-axis are observed with variable spacing (in terms of numbers of groups of tunnels between the faults). Of course, this defect is interesting and, based on a predictive approach, may help to synthesize new related materials, as already observed in several families of compounds such as tungsten bronze  $WO_{3-x}^{33}$  or in the  $(Pb,Bi)_{1-x}Fe_{1+x}O_{3-y}$  series.<sup>34</sup> These defects are probably related to a partial or inhomogeneous mixing with severe lithium loss/separation of reactants during the synthesis process. Thus, even if the starting powder has the expected Li:La:V ratio, any inhomogeneity would create regions with either rich or poor lithium content. In addition, Li loss may happen, because of sublimation or evaporation at high synthesis temperature (lithium evaporation occurs at 950 °C and accelerates at 1050 °C<sup>35</sup>). As long as the cationic tunnels are not filled in the structure, the cationic backbone is probably modified and, as a consequence, the general periodicity is potentially locally changed.

**3.6.** Physical Characterization. 3.6.1. Catalytic Tests.  $KLa_5O_5(VO_4)_2$  is a potentially interesting compound for catalysis, because of both its redox character (given by the vanadium element that is well-known to be adaptive, in terms of the degree of oxidation) and its acid behavior (linked to the presence of lanthanum). Since redox and acid properties are key points for ethanol oxidation reaction, we used this reaction to test the catalytic properties. Pure powder sample was tested at different temperatures (250, 275, 300, 325, 350, and 375 °C). Figure 8 presents the evolution of the ethanol conversion as a



Figure 8. (a) Presentation of ethanol conversion and carbon balance for  $KLa_5O_5(VO_4)_2$  registered at different temperatures, and (b) selectivity to acetaldehyde and  $CO_2$ .

function of temperature for the title sample. For oxidation reactions, the ethanol conversion increases with the temperature but still remains very low, under 30%, even for the highest temperatures tested. During ethanol conversion, the catalyst acts in favor of acetaldehyde production, at least at 250, 275, and 300 °C. Above this temperature, the selectivity in acetaldehyde suddenly decreases, probably because of the coproduction of CO<sub>2</sub>, preventing the use of such a compound as an efficient catalyst. Anyway, as many new materials, this preliminary test was necessary to evaluate its capacity for further applications.

3.6.2. Luminescence. The photoluminescence emission (PL) and photoluminescence excitation (PLE) spectra of

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 $KLa_5O_5(VO_4)_2$  are shown in Figure 9. The PLE spectrum exhibits two broad peaks, centered at 295 and 338 nm,



**Figure 9.** Photoluminescence emission and photoluminescence excitation spectra of  $KLa_5O_5(VO_4)_2$  (inset shows a photograph of the sample under same excitation).

respectively. These bands are due to an absorption process within  $VO_4^{3-}$  groups starting at 370 nm (3.8 eV). In fact, the origin is the charge transfer (CT) of an electron between the 2p orbitals of oxygen and vacant 3d orbitals of  $V^{5+}$  in the  $\mathrm{VO_4}^3$ groups with tetrahedral symmetry.<sup>36,37</sup> In this case, the ground state is  ${}^{1}A_{1}$  and excited states are  ${}^{1}T_{1}$ ,  ${}^{1}T_{2}$ ,  ${}^{3}T_{1}$ ,  ${}^{3}T_{1}$ .<sup>38</sup> The two bands observed are explained for allowed transitions, i.e.,  $A_1 \rightarrow$  ${}^{1}T_{2}$  and  ${}^{1}A_{1} \rightarrow {}^{1}T_{1}$ .<sup>1</sup> The PL spectrum, monitored at 338 nm, presents two intense peaks, centered at 466 and 495 nm, that can be attributed to  $({}^{3}T_{2}, {}^{3}T_{1} \rightarrow {}^{1}A_{1})$  transitions, respectively. However, these transitions are forbidden in the ideal  $T_d$ symmetry by the spin selection rule. Nevertheless, the structural study of the compound has highlighted a distortion of VO<sub>4</sub><sup>3-</sup> tetrahedron (V–O bond lengths between 1.582 Å and 1.729 Å). It is coherent with a lowering of the symmetry of the VO<sub>4</sub><sup>3-</sup> tetrahedron, compared to the ideal  $T_d$  symmetry. Consequently, the spin-forbidden transition is now allowed and explains the two bands observed.<sup>37</sup> It is known that the distortion enhances the spin-orbit interaction.<sup>39,40</sup>  $KLa_5O_5(VO_4)_2$  phosphor presents interesting blue-emitting properties under UV excitation (see inset picture in Figure 9), which may be useful for developing new color light sources, photoluminescent display devices, or UV sensors. To conclude, it would be also interesting to introduce another lanthanide (having electrons in the 4f orbital) on the  $La^{3+}$  sites in order to able to elaborate new phosphors emitting in the multiple visible spectral ranges.

# 4. CONCLUSION

This paper is the first example of the possibility to solve, and accurately refine, the crystal structure *ab initio* from precession electron diffraction tomography data, using the dynamical diffraction theory, and it shows how this new approach can help solid-state chemists to isolate new architectures with the ulterior motive of finding new materials. The model refined from PEDT data was shown to be superior to the model obtained by Rietveld refinement on powder X-ray diffraction data. The model was validated by density functional theory calculations. The structure analysis leads us to evidence a new series of compounds with potentially interesting optical properties. The title compound is a new oxo-centered material, based on  $OLa_4$  building units connected together to build twodimensional Cresnel-like layers surrounded by vanadate groups that form tunnels hosting the K<sup>+</sup> cation. In the literature, other materials have been described with related Cresnel-like layers but with various geometries observed for different unifying cations (Bi<sup>3+</sup>, Pb<sup>2+</sup>, etc.). From a methodological point of view, it encouraged us to diversify the nature of cations in order to obtain new architectures and attain other types of properties.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.5b02663.

Additional tables, showing a comparison between interatomic distances using different refinements (PDF) Crystallographic data for  $KLa_5O_5(VO_4)_2$  (CIF)

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#### Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

The Fonds Européeen de Développement Régional (FEDER), CNRS, Région Nord Pas-de-Calais, and Ministère de l'Education Nationale de l'Enseignement Supérieur et de la Recherche are acknowledged for funding X-ray and TEM facilities. This work was carried out under the framework of the Multi-InMaDe project supported by the ANR (Grant No. ANR 2011-JS-08 003 01). The authors thank Dr. Mickael Capron, Georgiana Bucataru, and Anita Borowiec for catalytic measurements.

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