Microstructural evolution of layered K-doped RuCl$_3$ during annealing traced by thermogravimetric analysis and 3D electron diffraction

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Microstructural evolution of layered K-doped RuCl$_3$ during annealing traced by thermogravimetric analysis and 3D electron diffraction


Dedicated to Professor Michael Ruck on the Occasion of His 60th Birthday

Nanoscale phase separation was induced in the K-doped RuCl$_3$ van der Waals material by annealing, and studied with the goal to find a natural design strategy for the formation of two-dimensional architectures as an alternative to the costly and time-consuming experimental artificial growth methods. Phase conversion was traced by means of thermogravimetric analysis combined with mass spectrometry. The local crystal structure of co-existing K$_x$Ru$_2$Cl$_6$ domains with the sizes of about 100 nm was solved by 3D electron diffraction.

Introduction

In recent years, there has been a great effort to create artificial heterostructures and nanoarchitectures using vertically stacked two-dimensional (2D) van der Waals (vdW) layered materials.\cite{1–3} Similar to those in bulk materials, defects or a lattice mismatch in 2D heterostructures can induce strains that distort the shape of individual layers or induce twists between the layers. However, the impact of defects is exacerbated with reduced dimensionality which may result in unique architectures, such as e.g. supertwisted spirals of layered materials,\cite{4,5} nanoscrolls, nanotubes and many others.\cite{6}

Fabrication of heterostructures has relied mostly on artificial growth methods, such as mechanical exfoliation and re-assembly, or chemical vapor deposition (CVD). Especially for the CVD method, all synthesis parameters have to be extremely precise since the desired architectures are often thermodynamically unfavorable.\cite{7} However, during annealing, many solids naturally undergo formation of morphologic microstructures or a phase separation, when, below a certain critical temperature, the components separate into distinct homogeneous regions with different physical and chemical properties. These precipitates may already have a complex spatial organization, e.g. 3D nanoscale strips in the alkali-doped iron selenides\cite{8,9} or arrays of nanocrystals coherently embedded into a semiconductor matrix.\cite{10} Moreover, creating boundaries between chemically distinct but structurally related phases may remarkably affect physical properties. For example, increased dislocation densities and decreasing grain size in thermoelectric materials may lead to reduced lattice thermal conductivity.\cite{11,12} In semiconductors, such as GaAs, GaN, ZnTe, or elemental semiconductors, e.g., Ge doped with transition metal ions (Cr, Mn, or Fe), the formation of self-assembled quantum dots or nano-islands with the composition differing from that of the matrix is strictly correlated with the presence of high-$T_c$ ferromagnetism, and has been extensively studied for potential applications in low-current semiconductor lasers, solar cells, single-photon emitters and detectors, quantum processors, and memories.\cite{13} Spinodal decomposition is proposed for stabilizing self-assembled interfaces between topological insulators by combining layers of iso-structural TIBIX$_x$ (X=S, Se, Te) materials. The tuning may induce phenomena such as topological interface states, non-trivial spin texture, and Rashba-like states.\cite{14} The broad variety of domains forming at micro- or nanoscale during the chemical decomposition poses significant challenges to elucidating their crystal structure, which is essential to understand their chemical and physical behavior. Conventional in-house structure characterization techniques, such as X-ray diffraction, often prove impractical in addressing this issue. To overcome these...
challenges and achieve structural elucidation at the nanoscale, we have employed three-dimensional electron diffraction (3D ED). This advanced method has gained recognition for its ability to determine the crystal structure of individual micro- and nanosized crystals.

This study contributes to the understanding of the boundary structures arising in K-doped RuCl₃ through a decomposition process. The system’s choice was motivated by an existing scope of studies showing that electrochemical intercalation of potassium into the RuCl₃ van der Waals material is very feasible and yields environmentally stable products. It has been tackled in the literature since the 1980s. Previous investigations focused largely on the reaction mechanisms, pH- and temperature dependencies, and the optical, optoelectronic, and transport properties of the intercalation products, e.g. K₃Ru₂Cl₆ (1 ≤ x ≤ 2) and to a significantly lesser extent on its crystallographic peculiarities. Whereas our structural studies of the K₃Ru₂Cl₆ intercalates and, in particular, of K₃Ru₂Cl₆ are described elsewhere,[20,21] this work examines the thermal decomposition of the K-intercalated RuCl₃ and compares it to the parent α-RuCl₃ compound. We find that decomposition of the intercalate markedly differs from that of α-RuCl₃, and notably, is accompanied by a nanoscale phase separation. Further, we focus on the detailed characterization of a new decomposition product by employing 3D ED, and a combination of the powder X-ray diffraction (pXRD), the thermogravimetric analysis combined with the mass spectrometry (TGA-MS), and the high resolution transmission electron microscopy (HRTEM). We unveil the crystal structure of a distinct K₃Ru₂Cl₆ domain arising from the decomposition process. The accurate structure elucidation helps to attain a more profound knowledge of the decomposition process in general.

Results and Discussion

After a rapid, high-temperature annealing of K-doped RuCl₃ following the procedure described in the Experimental Section, we analyzed the sample by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDX). SEM images of the annealed and non-annealed samples are shown in Figure 1.

The average quantitative composition of the samples before and after the annealing was determined by EDX. Annealing under vacuum leads to a drop of oxygen content in the specimen from approx. 16(5) at% to approx. 6(1) at%, but it also affects the K:Ru:Cl ratio in the sample, which changes from 0.77(8) : 1 : 3.03(10) to 0.55(3) : 1 : 2.45(7). In order to get further insight into it, we went for local analysis by TEM and 3D ED, described below in the manuscript.

A transmission electron microscopy (TEM) investigation reveals an inherent nanoscale phase separation in the annealed K-doped RuCl₃, visible at high resolution in the form of small, nanometer-sized plates in the annealed sample, not present in the non-annealed one. Thus, phase separation was induced in the K-doped RuCl₃ by annealing. To collect the structural information from these small domains, we have implemented 3D ED following the cRED protocol,[22] which allows structure reconstruction from a sequence of electron diffraction patterns recorded at different specimen tilt angles. TEM parallel beam nanoprobe mode was used to minimize the data collection region. Figure 2 shows a typical HRTEM image of the co-existing areas and their characteristic fast Fourier transform images (FFT). Region B is more extended, and its FFT pattern shows a distorted hexagonal array. In contrast, Region A is a relatively small domain embedded in the matrix of Region B, and its FFT pattern exhibits several rows of spots.

Small round particles seen on the surface are mainly Ru nanoparticles, as evidenced by EDX, whereas plate-like particles represent an unknown crystalline contamination.

We found out that the characteristic fast Fourier transform image from Region B is consistent with an ED of (001) crystal planes in the crystal structure of the rhombohedral K₃Ru₂Cl₆ intercalate, in line with our pXRD results (see below).

Next, we analyzed the reconstructed 3D reciprocal space from Region A, demonstrating rows of reflections with a d-spacing of 1.7 nm in FFT. This d-spacing is present neither in K₃Ru₂Cl₆ nor in the parent α-RuCl₃. The domain of the unknown phase is oriented relatively close to a zone-axis and thanks to it is clearly visible among the surrounding matrix of K₃Ru₂Cl₆ due to a HRTEM diffraction contrast. A slightly larger domain of the same phase with sizes of about 50×70 nm seen in the direct space image in Figure 3 was used further for the 3D ED data collection.

Although the dataset was noisy, a hexagonal unit cell with lattice parameters a = 6.717(3) Å, c = 17.096(2) Å, V = 668.0(2) Å³ was found by the RED₃ cell finding algorithm from the 3D ED experiment. The only condition l = 2n was found in the 00l reflection row, suggesting possible space groups: P6₃mc, P62c and P6₃/mmc. Similar cell parameters are commonly adopted by halides crystallizing in a derivative of the hexagonal perovskite (ABX₃) structure, with B cations occupying only two-thirds of the octahedral site (i.e., A₁B₂X₆), such as for example Cs₃β₂Cl₆ (B = Mo, Fe, Cr).[23,24] An isostructural Cs₅Ru₂Cl₆ compound was described by Darriet.[25] Early mentions of K₃Ru₂Cl₆ as a precursor for synthesizing diruthenium complexes[26–28] did not include any crystallographic characterization. In the PhD thesis of S. Hartwig (Universität Bayreuth), the K₃Ru₂Cl₆ phase was isolated and its cell parameters were estimated from pXRD, but no crystal structure model was provided.[29] Our
ab-initio structure solution from the 3D ED data confirmed that K₃Ru₂Cl₉ is isostructural to Cs₃Ru₂Cl₉ (sp. gr. P6₃/mmc). Out of 2294 reflections collected, 217 were unique, R_int = 0.289. The resolution cutoff of 0.79 Å was chosen based on Ref. [30] (CC1/2 = 98.4 and 88% in the resolution shells 0.83 and 0.79 Å, correspondingly), and the resulting total data completeness was 66.1% and I/σ(I) = 4.73. The refinement based on 217 reflections and 19 parameters converged to R = 0.179 and wR² = 0.454. Details of the refinement are given in Table 1. CCDC 2274900 contains the crystallographic data for the solved K₃Ru₂Cl₉ structure. Due to a strong peak overlapping (see Figure 6) and small size of the domains, this phase cannot be reliably identified from pXRD, however, it can be discovered by 3D ED.

**Figure 2.** A typical HRTEM image of the annealed K-doped RuCl₃ specimen showing co-existing crystalline domains. Matrix domain (m) is imaged along the [001] direction, domains of K₃Ru₂Cl₉ (d) – close to the [010] direction in the K₃Ru₂Cl₉ crystal structure.

**Table 1.** Crystal data and structure refinement for K₃Ru₂Cl₉.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>K₃Ru₂Cl₉</td>
</tr>
<tr>
<td>Formula weight</td>
<td>638.51</td>
</tr>
<tr>
<td>Temperature/K</td>
<td>293(2)</td>
</tr>
<tr>
<td>Crystal system</td>
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<tr>
<td>Space group</td>
<td>P6₃/mmc</td>
</tr>
<tr>
<td>a/Å</td>
<td>6.717(3)</td>
</tr>
<tr>
<td>c/Å</td>
<td>17.096(2)</td>
</tr>
<tr>
<td>Volume/Å³</td>
<td>668.0(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>ρ calc/g cm⁻³</td>
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</tr>
<tr>
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</tr>
<tr>
<td>Radiation</td>
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</tr>
<tr>
<td>2Θ range for data collection/°</td>
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</tr>
<tr>
<td>Reflections collected</td>
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</tr>
<tr>
<td>Independent reflections</td>
<td>217 [R int = 0.289, R sym = 0.160]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>217/0/19</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.606</td>
</tr>
<tr>
<td>Final R indexes (I ≥ 2σ(I))</td>
<td>R₁ = 0.179, wR₂ = 0.454</td>
</tr>
<tr>
<td>Final R indexes [all data]</td>
<td>R₂ = 0.208, wR₂ = 0.467</td>
</tr>
<tr>
<td>Largest diff. peak/hole/e Å⁻³</td>
<td>1.67/−2.37</td>
</tr>
</tbody>
</table>

The structure is characterized by isolated dimeric [Ru₂Cl₉]³⁻ units, Figure 4A. In contrast to K₃Ru₂Cl₉ or α-RuCl₃ which host layers of edge-sharing [RuCl₆] octahedra with the central Ru³⁺ ions forming a honeycomb lattice, the structure of [Ru₂Cl₉]³⁻ units is not 2D anymore, and results from the sharing of a trigonal face between two [RuCl₆] octahedra. The Ru atoms are located close to the centers of their respective coordination octahedra, with the shortest Ru–Ru distance of 2.59(3) Å.

**Figure 3.** 3D ED dataset taken from a single domain of the annealed specimen revealing a hexagonal unit cell with a = 6.717(3) Å, c = 17.096(2) Å. The scalebar 5 nm is the same for all ED images.
Following the inherent phase separation and identification of nanometer-sized platelets with the composition \( K_2 RuCl_6 \) in the TEM after rapid annealing, an investigation was carried out to determine whether the formation of this phase also occurs in the course of the thermal decomposition of \( K_2 RuCl_6 \).

At first, a \( K_2 RuCl_6 \) sample obtained by electrochemical intercalation was measured by pXRD (Figure 6). The most prominent reflections for the non-annealed sample can be indexed in a rhombohedral cell with the lattice parameters \( a \approx 3.46(2) \, \text{Å} \), \( c \approx 24.96(2) \, \text{Å} \). This structure adopting the space group \( \text{R}3 \) is the subject of our other work that deals with the structural aspects of the non-annealed \( K_2 RuCl_6 \) intercalates (1 < \( x < 2 \)).\(^{[20,21]}\) The structure preserves the \( \text{BiI}_2 \)-type layers of edge-sharing \( [\text{RuCl}_6] \) octahedra with the central \( \text{Ru} \) ions forming a honeycomb lattice and additionally hosts a varying amount of K atoms in the interlayer space. Despite the increased ionic interaction between the layers via K cations, the \( K_2 RuCl_6 \) structure is a subject to multiple stacking faults due to the sliding of the layers with respect to each other. It is worth noting that for the sample before the TG, the first pXRD peak splits into two, with the \( d \) values of \( \sim 8.32 \, \text{Å} \) and \( \sim 8.21 \, \text{Å} \), indicating an intrinsic inhomogeneous potassium distribution in the sample.

The thermal behavior of the \( K_2 RuCl_6 \) (\( x = 1–2 \)) samples with variable potassium doping was investigated by thermogravimetric analysis coupled with mass spectrometry (TGA-MS) to get further information about the gaseous decomposition products formed.

As references, \( \text{RuCl}_3 \) and \( \text{KCl} \) were also analyzed by TGA under the same conditions. The obtained TG curves and their first derivatives (DTG) are shown in Figure 5A. The measurement was stopped at certain temperatures to identify the steps that occur during the heating from room temperature to 1100°C (Figure 5B). An optical examination and identification of the crystalline phases by powder diffraction (pXRD) of the crucible residue (see Figure 5B), were performed. Diffractograms and the assignment of the crystalline phases can be taken from Figure 6.

The thermal decomposition of \( K_2 RuCl_6 \) (\( x = 1–2 \)) runs in six defined steps. The first step starts at \( T_{\text{onset,DTG}} = 473 \, ^\circ \text{C} \) (\( T_{\text{peak,DTG}} = 545 \, ^\circ \text{C} \) and ends with a mass loss of 17.05% at 568°C. Up to 473°C, no gaseous species could be detected by MS (Figure 5B). It can therefore be assumed that the \( K_2 RuCl_6 \) (\( x = 1–2 \)) under investigation is completely anhydrous (\( m/z = 17, 18 \)). Atomic chlorine species of both isotopes, \( ^{35} \text{Cl} \) and \( ^{37} \text{Cl} \), were detected in the ratio 1 to 3 at the beginning of the decomposition of \( K_2 RuCl_6 \) while the molecular chlorine species did not occur. The observed mass traces of \( ^{36} \text{HCl} \) and \( ^{38} \text{HCl} \) in the ratio 1 to 3 can be explained by the reaction of formed gaseous \( ^{35} \text{Cl} / ^{37} \text{Cl} \) with the small traces of water (<0.02 ppm) from the purge gas.

According to the evaporation behavior of pure \( \alpha \text{RuCl}_3 \) simulated by detailed Calphad-modelling,\(^{[31]}\) it can be assumed, that the first TG step, starting from 473°C, leads to partial decomposition of \( K_2 RuCl_6 \) under slight loss of chlorine and small amounts of \( \text{RuCl}_3 \) thus leading to an enrichment of potassium. The early start of decomposition, compared to the

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**Figure 4.** (A) Crystal structure of \( K_2 RuCl_6 \). K, Ru and Cl atoms are shown in yellow, grey and green, respectively. (B) Electronic band structure (left) and density of states (DOS, right) for \( K_2 RuCl_6 \). Selected projected contributions to the DOS are indicated.

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between the atoms in the adjacent octahedra. The Ru–Cl bond lengths are in the range of 2.25–2.29 Å.

To gain insight into the electronic properties of \( K_2 RuCl_6 \), which was present in our samples only as nanoscale domains, we carried out first-principle calculations using the experimentally determined crystal structure. Due to the 4d electronic state of \( \text{Ru}^{3+} \) in \( K_2 RuCl_6 \), a magnetic ground state can be anticipated. Therefore, we started our calculations by considering a ferromagnetic structure. However, the local magnetic moments on the Ru atoms converged to less than \( 10^{-3} \, \mu_B \), indicating the absence of localized magnetism. A calculation for an antiferromagnetic arrangement also converged to negligible magnetic moments on the Ru sites, thus confirming a non-magnetic ground state. This result aligns with the experimental observations on the related compound, \( \text{Cs}_2 \text{Ru}_3 \text{Cl}_6 \), which only showed a weak paramagnetic response.\(^{[25]}\)

The lack of localized magnetism is related to the formation of a Ru–Ru bond in the \( [\text{Ru}_2 \text{Cl}_6]^{3-} \) dimers, resulting in a singlet ground state. The observed weak paramagnetism at finite temperatures is ascribed to the population of the excited triplet state. The band structure and electronic density of states for \( K_2 RuCl_6 \) are shown in Figure 4B. The ground state is hallmarkd by an indirect bandgap of about 0.56 eV. Due to the ionic nature of the K–Cl interaction and the accompanying electron transfer from the K atoms, the contribution of the K valence states around and below the Fermi level (\( E_F \)) is small. The DOS region below the \( E_F \) mainly comprises the hybridized Ru(4d) and Cl(3p) states. The localized bands right above the Fermi level consist predominantly of the unoccupied Ru(4d) \( e_g \) states.
Figure 5. Analysis of the thermal decomposition of K₃Ru₆Cl₆ by TGA-MS under helium atmosphere at a heating rate of 1 K·min⁻¹ (A): TG-, DTG-curves of K₃Ru₆Cl₆ (black), RuCl₃ (red) and KCl (blue), and (B): TG-curve of K₃Ru₆Cl₆ with the identified mass changes (grey), phase compositions from pXRD (blue) of the crucible residue at 500 °C, 660 °C, 850 °C and 1100 °C and the corresponding MS-spectrum of formed gaseous species over the whole temperature range.

pure RuCl₃ phase (see Figure 5A), hints to a metastable state of K₃Ru₆Cl₆.

Powder XRD of the residue after stopping the TG measurement at 500 °C showed a presence of α-RuCl₃ and presumably a potassium-rich K₃Ru₆Cl₆ phase. Figure 6 shows that the most prominent reflections in the diffractogram at 500 °C fit well to their (00l) series. Both α-RuCl₃ and intercalated K₃Ru₆Cl₆ exhibit high texture effects due to their layered morphology. Compared with the non-annealed sample, the d-spacing for the first pXRD peak increases to ~8.52 Å. It presumably corresponds to the K₃Ru₆Cl₆ intercalated phase with an increased c-axis parameter and higher K-content. Interestingly, the appearance of α-RuCl₃ phase at 500 °C might result either from non-uniform intercalation or might indicate redistribution of K in the sample, e.g. formation of regions rich in the K-content, and deintercalated regions.

The first decomposition step is immediately followed by the second and third decomposition steps, thus forming an actually long drawn, but segmented decomposition profile. The second decomposition step of K₃Ru₆Cl₆ (x = 1–2) could be determined at θ onset,DTG = 497 °C (θ peak,DTG = 589 °C) with the mass loss of 5.02% and the end temperature at 607 °C. The third mass stage starts at θ onset,DTG = 575 °C (θ peak,DTG = 637 °C) with a mass loss of 4.81% and ends at 661 °C. Here, the intercalated phase completely decomposes, forming KCl and Ru components resulting from the incongruent decomposition under release of chlorine.

This behavior completely agrees with the one of pure RuCl₃, which decomposes starting from θ onset,DTG = 565 °C (θ peak,DTG = 619 °C).

According to the calculated gas phase composition,[31] mainly Cl (from Cl₂) as gaseous species could be identified with the MS of RuCl₃ and finally, for the investigated samples K₃Ru₆Cl₆ (x = 1–2) as well. RuCl₃ could not be identified in the MS, as small amounts of the gas species already condense in the transfer line. The pXRD analysis of the crucible residue of K₃Ru₆Cl₆ (x = 1–2) decomposed up to 660 °C indicates the formation of the following phases: KCl, Ru, and RuO₂ (Figure 6). Examination of the crucible residue of RuCl₃ after the first mass step (700 °C) resulted in the identification of Ru and RuO₂ (Figure 6). Thus, within the second and third mass stages further decomposition of the potassium-rich K₃Ru₆Cl₆ phase to KCl(s) and decomposition of RuCl₃(s) to Ru(s) and Cl₂(g) occurs. The detection of RuO₂(s) in the pXRD (Figure 6) can be explained by...
the reaction of Ru with the small traces of oxygen (<0.01 ppm) in the He purge gas stream.

The fourth decomposition step with a mass loss of 10.74% is observed in the temperature range from 662 °C to 773 °C (\(\vartheta_{\text{onset, DTG}} = 693 °C\), \(\vartheta_{\text{peak, DTG}} = 759 °C\)). No signals from \(^{21}\text{Cl}\) and \(^{31}\text{Cl}\) could be detected in this temperature interval by MS. The pXRD of the sample decomposed up to 850 °C showed the crystalline phases of Ru and RuO₂. The reference measurement of the pure KCl shows an initial shoulder at \(\vartheta_{\text{onset, DTG}} = 701 °C\), with a subsequent sharp loss of mass at \(\vartheta_{\text{peak, DTG}} = 775 °C\) (\(\vartheta_{\text{peak, DTG}} = 795 °C\)). This behavior corresponds to the initial melt of the KCl, with the following immediate sublimation to KCl(g). Here again, the released KC\(_{\text{liq}}\) mainly condenses in the transfer line to the MS. Nevertheless, in agreement with the onset temperatures of the melt and subsequent vaporization of KCl as well as the results of pXRD, the fourth mass stage of thermal decomposition of K\(_2\)RuCl\(_6\) (\(x = 1–2\)) can be attributed to the sublimation of KCl.

The fifth mass step of K\(_2\)RuCl\(_6\) (\(x = 1–2\)) reveals a slight mass increase of \(+0.37%\) in a temperature range from 773 °C to 883 °C, which is also indicated in the reference measurement of pure RuCl\(_3\). Analysis of the solid residue of the sample of K\(_2\)RuCl\(_6\) (\(x = 1–2\)) in the crucible after 850 °C by pXRD shows the formation of RuO₂ (Figure 6). An optical examination of the solid (Figure 7A) confirms formation of grey RuO₂ layer. Thus, it is probable that the formed Ru was oxidized by the small traces of oxygen in the He purge gas flow.

The sixth and last mass step shows a mass loss of 13.14%. The decomposition step proceeds in the temperature range from 883 °C to 1100 °C with \(\vartheta_{\text{onset, DTG}} = 989 °C\) and \(\vartheta_{\text{peak, DTG}} = 1060 °C\). This decomposition step corresponds to the third effect of the pure RuCl\(_3\) (\(\vartheta_{\text{onset, DTG}} = 987 °C\), \(\vartheta_{\text{peak, DTG}} = 1039 °C\)). The pXRD of the crucible residue of K\(_2\)RuCl\(_6\) and RuCl\(_3\) obtained at temperature up to 1100 °C reveals only reflections of Ru (Figure 6). It is additionally proven by the formation of gold-colored porous solid after heating of K\(_2\)RuCl\(_6\) up to 1100 °C (Figure 7B). Concluding, the last step can be assigned for both K\(_2\)RuCl\(_6\) and RuCl\(_3\) to the reduction of the previously formed RuO₂ with the formation of Ru. Similar behavior of mass increase by oxidation with the oxygen from the purge gas and subsequent reduction has already been described for rhodium.

Albeit exact quantification of the observed decomposition path was hindered due to the uncertainty of the initial solid and the complex composition of the gas phase during the thermal treatment, observations indicate occurrence of mainly Cl\(_2\)(g) and KCl(g), but simultaneously release of RuCl\(_3\)(g) and O\(_2\)(g), too. This study concludes that K\(_2\)RuCl\(_6\) does not form, at least not as a bulk phase with visible contributions to pXRD and TGA, upon thermal decomposition of K-doped RuCl\(_3\) at the heating rate of 1 K·min\(^{-1}\). Nanoscale phase separation we report here is thus, presumably, the result of a non-equilibrium process facilitated by rapid, high-temperature heating.

**Conclusions**

In this paper we study the processes of thermal decomposition of K-doped RuCl\(_3\) by combining the pXRD, TGA-MS, HRTEM and electron diffraction findings. It was shown that the decomposition of K-doped RuCl\(_3\) to Ru and KCl(g) occurs in a multi-step fashion in the temperature range 400–1100 °C and is accompanied by elimination of Cl\(_2\). In the temperature range approx. 500–600 °C, a nanoscale phase separation can be naturally induced by rapid, out-of-equilibrium heating, revealing itself in HRTEM as structurally different plate-like domains embedded into the K\(_2\)RuCl\(_6\) matrix. The crystal structure of the domains was solved and refined against 3D ED data. The structure was found to adopt the sp.gr. \(P\_6_3/mmc\) with the unit-cell parameters \(a = 6.717(3)\) Å, \(c = 17.0962(2)\) Å, \(V = 668.02(2)\) Å\(^3\) and has a general formula K\(_x\)RuCl\(_6\). The comprehensive nano-characterization has enabled us to put on a firmer basis the
origin of crystallographic and chemical phase separation observed during annealing of the K-doped RuCl₃ intercalate. Our study demonstrates the power of 3D ED in tackling the challenges of structural elucidation in systems undergoing nanoscale phase separation, contributing to the advancement of scientific knowledge and potential practical applications in the field of materials research.

**Experimental Section**

Large crystals of RuCl₃ for intercalation were grown by the chemical vapor transport technique as described elsewhere. The mechanism of CVT for α-RuCl₃ is described in detail in Ref. [31] α-RuCl₃ used for the thermogravimetric analysis was purchased from Aldrich Chemistry (45–55 % Ru content), and purified according to Froeschke et al.[36] Intercalation was performed at room temperature in a three-electrode electrochemical cell filled with 0.5 M KCl (99 %, Sigma-Aldrich) aqueous solution. A rectangular piece of α-RuCl₃ with the sizes of about 2×3 mm was placed onto the Pt mesh (99.9 %, Goodfellow GmbH) that was then folded around the crystal and clamped. A Pt plate (99.99 %, Goodfellow GmbH) was used as the counter (CE) electrode and an Ag/AgCl wire as a pseudo-reference electrode. Metrohm Autolab PGSTAT204 potentiostat with the Nova 2.1.5 software was used for the control of the measurements and for the acquisition of the data. Intercalation was performed in a chronoamperometric regime by applying a constant potential of −0.6 V vs Ag/AgCl pseudo-reference electrode for 5 minutes. After the electrochemical treatment was accomplished, the K-doped RuCl₃ crystal was washed with distilled water and dried in air for a few days. Annealing of the K-doped RuCl₃ crystal was conducted in a quartz tube heated by a conventional hydrogen burner under dynamic vacuum (10⁻³ mbar) for several seconds.

The thermal decomposition of synthesized KₓRu₃Clₓ-KCl (99.5 %, Carl Roth GmbH + Co. KG), and RuCl₃ (45–55 % Ru content, Aldrich Chemistry, purified according to Froeschke et al.[36]) was investigated with a simultaneous thermal analyzer STA 449 F3 Jupiter combined with a mass spectrometer QMS 403 D Aäolos (TGA/DTA/MS) manufactured by NETZSCH. The measurements were carried out in the temperature range from 40 °C to 1100 °C at a heating rate of 1 K·min⁻¹ under the helium flow with a rate of 50 cm³·min⁻¹ and 20 cm³·min⁻¹ inert gas flow for the balance. Alumina crucibles without cover were used. The adapter head of the STA was heated to 300 °C as well as the transfer line between STA and QMS and the inlet of QMS. Initially, the bargraph and after MID measuring mode for the measurement. All measurements were done at room temperature under an air atmosphere. For the acquisition, the obtained diffractograms were analyzed for the contained phases using EVA software. Reference samples from the ICDD database were used for phase identification.

The specimen for 3D ED and HRTEM experiments was prepared by crushing a crystal of the annealed K-doped RuCl₃ in a mortar, followed by suspending it in ethanol. Drops of the suspension were then dried on carbon-film copper grids (Cu150P Okenshjo Co., Ltd) at room temperature. 3D ED patterns and HRTEM images were collected on a probe and image C1 – corrected Themis Z microscope operating at 300 kV and equipped with a Gatan OneView camera. In-situ data capture mode with 1024×1024 pixels resolution (binning ×4) was employed. Data acquisition was performed using a single-tile tomography holder, following the cRED protocol[41] and was controlled by InsteaDmatic script.[42] ED frames were collected over a tilt range of ±40 ° with a rotation speed ~0.43°/s, the exposure time was 0.3 s. Diffraction frames were processed with the XD[36] The structure was solved by dual-space phasing in SHELXT[43] and refined by full-matrix least-squares method on F² with SHELXL[44] using Olex2 software.[45]

Electronic structure calculations on the density functional theory level (DFT) were performed with the FPL021.00 code.[46] The Perdew-Wang (PW92) flavor of the local density approximation (LDA) functional was used.[47] To account for the electronic correlations, the LDA+U scheme was applied, with the on-site Coulomb repulsion U = 1.5 eV and Hund’s exchange J = 0.3 eV, as has been used for α-RuCl₃ in previous publications.[43,48] The Brillouin zone was sampled by a 8×8×3 k-point grid after checking for convergence.

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**Conflict of Interest**

The authors declare no conflict of interest.

**Data Availability Statement**

The data that support the findings of this study are available from the corresponding author upon reasonable request.
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