



Synthesis and Characterization of Binary Azides (e.g. RbN_3) via Ion-Exchange Method

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Abstract: Azides have garnered significant interest in chemical research for their diverse properties and applications, ranging from their use in airbags and detonators to their roles in photochemistry. Despite this attention, there remains a dearth of detailed studies focusing on the synthesis and characterization of binary azides. In this study, a robust and safe method for the synthesis of RbN_3 via ion exchange is presented, addressing the inherent challenges associated with handling highly explosive alkali metal azides. The experimental procedure, conducted under stringent safety measures, resulted in the successful production of high-purity RbN_3 , as confirmed by X-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy analyses. XRPD data with the reference intensity ratio method (RIR) confirmed phase purity above 99 %, which is in good agreement with the elemental ratio found by SEM-EDX analysis. The synthesized RbN_3 exhibited crystalline white powder morphology, free from impurities, thus demonstrating the efficacy of the ion exchange approach. X-ray powder diffraction (XRPD) and Vibrational spectroscopy analyses provided additional insights into the structure and purity of RbN_3 in accordance with theoretical expectations; the characteristic vibrational modes for N_3^- could be well found at the expected theoretical and experimental ranges. These findings show an easy, safe, and reliable method for synthesizing binary azides and contribute to a deeper understanding of azide chemistry, with implications for various scientific disciplines.

Keywords: Azides, Ion-Exchange, Vibrational Spectroscopy.

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1. INTRODUCTION

Azides were first discovered 100 years ago, and since then, they have received great attention due to their interesting chemistry and properties, such as shock and friction sensitivity and explosive and energetic nature. With such properties, the applications of azide compounds are rich from the binary azides (e.g., NaN_3) in the fields of nitrogen sources, airbags, detonators, and biocides to the Heteroleptic complex (C_6H_5)₃PAu^I[N_3] in the field of photochemistry (1). The research on azide chemistry is also vast and contains many examples of Homoleptic Azido Complexes (1-6) and Heteroleptic Azido Complexes (7-9). The azide ion (N_3^-) acts as a terminal and a bridging ligand in these complexes, as shown in the literature (10,11).

The azide chemistry was thoroughly investigated by Beck et al. starting in the 1960s (5). More recently,

Haiges discussed the syntheses, properties, and crystal structures of various metal oxopolyazides (12). The coordination properties of the first binary titanium azides, including $[\text{Ti}(\text{N}_3)_4]$, $[\text{Ti}(\text{N}_3)_5]^-$, and $[\text{TiN}_3)_6]^{2-}$ were investigated (13). Christie et al. also studied the crystal structure and vibrational spectroscopy of the binary zirconium and hafnium polyazides $[\text{PPh}_4]_2[\text{M}(\text{N}_3)_6]$ ($\text{M}=\text{Zr}, \text{Hf}$) (14). Polyazido adducts $[(\text{bpy})\text{Ti}(\text{N}_3)_4]$, $[(\text{phen})\text{Ti}(\text{N}_3)_4]$, $[(\text{bipy})_2\text{Zr}(\text{N}_3)_4]_2\bullet\text{bpy}$, and $[(\text{bipy})_2\text{Hf}(\text{N}_3)_4]_2\bullet\text{bpy}$ were recently reported by Saal and coworkers (15). Many other successful examples of the synthesis and characterization of rich azide chemistry can be found in a recent review article by Beck et al. (5). In most of these investigations, the binary azides of alkali metals such as LiN_3 , NaN_3 , KN_3 , RbN_3 , and CsN_3 that contain symmetric azide anions are used to synthesize the more complex compounds. These binary azides can be described as hard to handle, unstable, and decomposing when exposed to heat and light. Thus, it is important to obtain binary

azides using a safe and sound method. Most of the investigations use NaN_3 directly in acidic or solvent mediums to directly synthesize other binary azides or complex azides that can lead to impurities and safety hazards, and there is a lack of research in the detailed synthesis and characterization of binary azides (16-18). These methods specifically consist of reacting a soluble inorganic azide (usually NaN_3) with a soluble target compound salt, usually nitrate or acetate salts, in an aqueous solution, forming the target azide compound as a precipitate (19,20). However, in these methods, the precipitate could usually be contaminated with the cation originating from the educt azide (e.g., NaN_3) and the anion coming from the target azide educt (e.g., nitrate or acetate). In addition, there is a lack of research on alternative synthesis methods for binary azides in literature (5,16). Therefore, herein, the high-purity synthesis and characterization of RbN_3 via an ion exchange method are presented. As the soluble inorganic azide cation (e.g., Na^+) is trapped in the ion-exchange column, and carbonates would react to form $\text{CO}_{2(g)}$, leaving the reaction vessel, high purity can be obtained at the end by this method. Binary azide, RbN_3 , is first synthesized through a column ion exchange method, and the compound is later crystallized through the evaporation of a solvent medium. The synthesis and physical characterization, through X-ray powder diffraction, FTIR, and Raman spectroscopy, are reported in detail.

2. EXPERIMENTAL SECTION

2.1. Synthesis

Alkali metal azides have highly explosive natures, so all material handlings must be carried out with utmost care and under extreme safety cautions (e.g. protective shields, goggles, shock-resistant gloves etc.). Also, the minute amount of samples should be used in order to prevent damage in case of an explosion hazard. For the synthesis of alkali metal binary azides, first, the resin column ($l = 800$ mm, $\varnothing_i = 14$ mm) was filled with acidic cation-exchange resin (Merck). Then, the resin column was exchanged for an H^+ cycle using a 1M solution of H_2SO_4 . Distilled water was passed through the ion exchange column afterward to wash away the excess amount of H_2SO_4 . Afterward, NaN_3 (Merck 99.9 %) was dissolved in water to obtain a 2M solution; 2M solution of NaN_3 was then passed through the H^+ loaded ion exchange column, resulting in HN_3 (the drop rate of HN_3 solution is adjusted to 5 mL/min.) at the end of the column reacting with Rb_2CO_3 as shown in Figure 1.

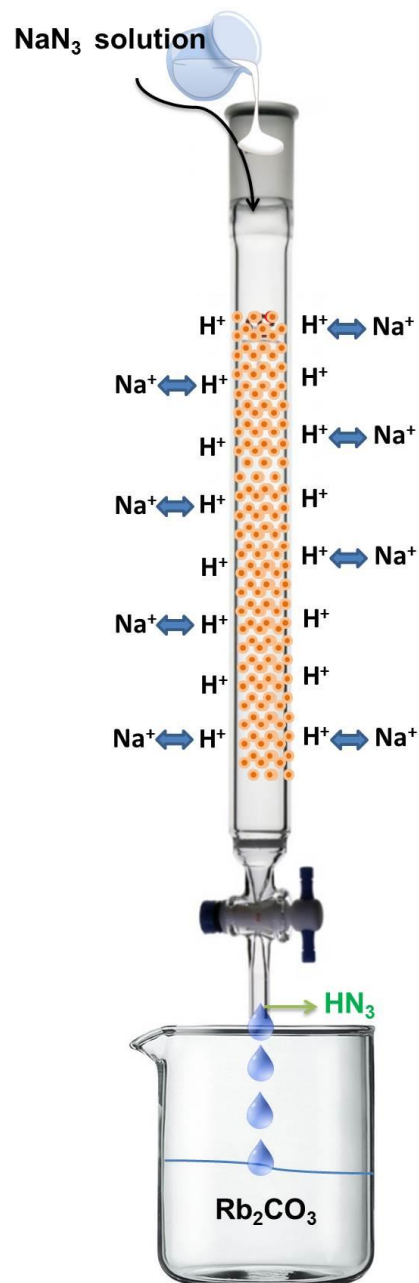


Figure 1: Synthesis scheme of RbN_3 via ion-exchange method.

In order to pass the newly formed HN_3 through the ion column to the end of the column, distilled water was added continuously on top of the column to keep the ion-exchange resin wet during the exchange. The formation of HN_3 at the end of the column was confirmed by checking the pH in different time intervals Table 1.

Table 1: pH control for HN_3 formation.

Time (minutes)	pH
0	6.8
5	6.5
15	5.7
20	4.9
25	4.1

The other binary azides chosen from alkali and earth alkali metals can also be synthesized similarly with the change of carbonate source. The completion of the reaction ($\text{Rb}_2\text{CO}_3 + 2\text{HN}_3 \rightarrow 2\text{RbN}_3 + \text{H}_2\text{CO}_3$) was controlled with the disappearance of any solid residue in the reaction and the pH control of the medium that should be in the range of $\sim \text{pH} = 4$. The white powder, RbN_3 was obtained at the end by the evaporation of the remaining solvent at 40-50 °C overnight. The evaporation temperatures above 50 °C should be prevented due to the explosive nature of azides.

2.2. Characterization

Fourier-transform infrared spectroscopy (FTIR) was measured with a Thermo Scientific Nicolet iS10 spectrometer (a single reflection diamond attenuated total reflectance (ATR) module). Renishaw Raman microscope equipped with a 532 nm laser as the excitation source was used to perform Raman spectroscopy. The phase and purity of RbN_3 were determined by X-ray powder

diffraction (XRPD) using a Rigaku MiniFlex X-ray diffractometer and $\text{Cu K}\alpha_1$ radiation (operated at 15 mA, 40 kV). Scanning electron microscope measurements were performed SEM, Thermo Fisher Quattro ESEM FE-SEM.

3. RESULTS AND DISCUSSION

At the end of the synthesis via the ion exchange method, a crystalline white powder was acquired. This powder was carefully ground in an agate mortar for the X-ray powder diffraction (XRPD) analysis, and excessive force was avoided during grinding to prevent the explosion of azides. The XRD powder pattern (XRPD) of the synthesized RbN_3 is shown in Figure 2. The XRPD pattern of RbN_3 synthesized via ion exchange method directly matches the theoretical pattern, and no impurity phases can be detected. The phase purity was found to be above $\sim 99\%$, which was calculated through the reference intensity ratio (RIR) method (21).

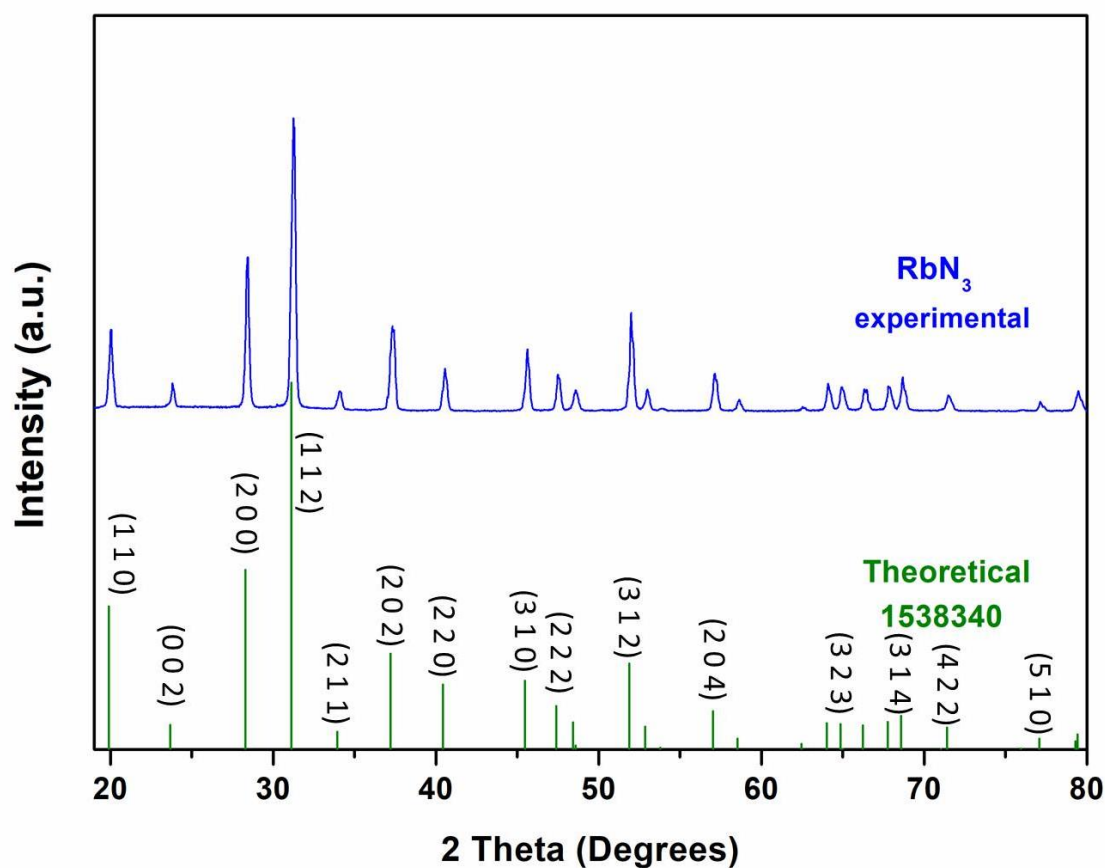


Figure 2: XRPD pattern of the ion-exchange synthesized RbN_3 vs the theoretical pattern (Crystallography Open Database no 1538340).

The vibrational spectroscopy analysis is in good agreement with XRPD analyses in terms of confirming the high purity of the RbN_3 phase after the synthesis and is also comparable to the NaN_3 phase. The common spectroscopic relevant unit in RbN_3 can be assigned as the discrete $(\text{N}_3)^-$ moiety with the symmetry $D_{\infty h}$. In line with this assignment, the vibrational spectra can be investigated in general within four well-separated wave regions (1,5,6,22). The vibrations' most common (N-N-N) stretching modes can be

distinguished into two separate sets of frequencies between $1200\text{--}1500\text{ cm}^{-1}$ and $1700\text{--}2100\text{ cm}^{-1}$. The range $500\text{--}800\text{ cm}^{-1}$ is dominated by in and out of plane (o.o.p.) deformations $\delta(\text{N-N-N})$ and $\gamma(\text{N-N-N})$ of the azido group. The valence and bending vibrations of the metal nitrogen bonds, as well as lattice vibrations, appear below 400 cm^{-1} , which cannot be clearly assigned due to their overlap in Raman spectra and device limitation in FTIR spectra.

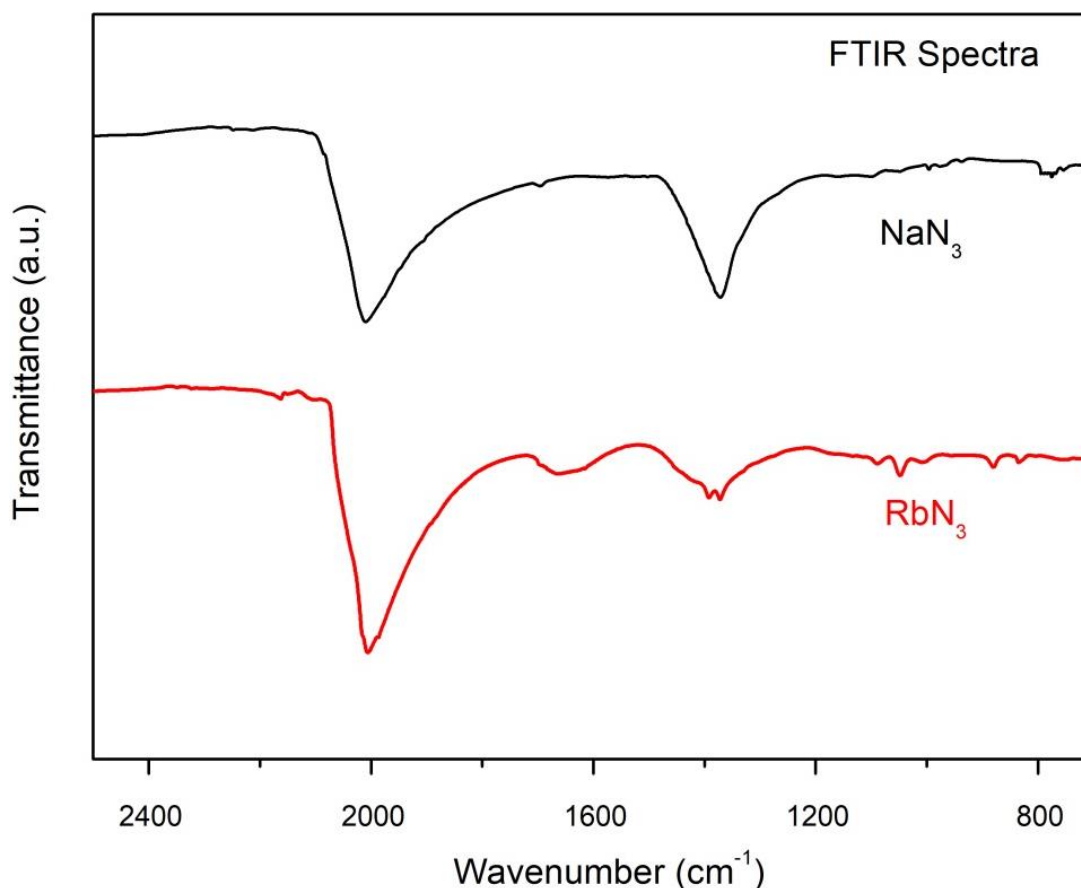


Figure 3: FTIR spectrum of the ion-exchange synthesized RbN_3 vs NaN_3 educt.

Specifically, the FTIR spectra of the synthesized RbN_3 and the comparison to the NaN_3 educt used for the synthesis are depicted in Figure 3. The valence modes for the azido group can be assigned to the peaks at $\sim 2010 \text{ cm}^{-1}$ and 1370 cm^{-1} . The peaks below 1000 cm^{-1} stem from the bending modes of the azide moiety, as well as from combination modes, and the findings are in alignment with literature findings (1,5,6). The valence and bending vibrations of the metal nitrogen bonds are expected to appear below $400\text{--}500 \text{ cm}^{-1}$, but they are not recorded due to the device measurement limitation.

The Raman spectra of the synthesized RbN_3 and the comparison to the NaN_3 educt used for the synthesis are depicted in Figure 4. Again, Raman spectroscopy analysis is in good agreement with XRPD and FTIR analyses in terms of confirming the high purity of RbN_3 phase after the synthesis, and also directly comparable to the NaN_3 phase confirming the reaction of Rb_2CO_3 with HN_3 producing RbN_3 . The peaks appearing at 1335 cm^{-1} and 1265 cm^{-1} in the Raman spectrum of RbN_3 can be assigned as the stretching modes of the azide group in RbN_3 (17). The valence and bending

vibrations of the metal nitrogen bonds are observed below 400 cm^{-1} in Raman spectra but are hard to distinguish due to the overlap in this region. Nevertheless, all analyses (XRPD, FTIR, and Raman) performed confirmed the successful synthesis via ion exchange method and revealed similar results in terms of the purity of the synthesized compound.

Scanning electron microscopy (SEM)-EDX analysis of the ion-exchange synthesized RbN_3 is depicted in Figure 5. The shape of the particles is not very well-defined, and the crystallite size of RbN_3 particles approximately ranges from $2 \mu\text{m}$ to $5 \mu\text{m}$. These crystallites seemingly form larger agglomerates in the range of 20 to 50 microns. The EDX analysis confirms the phase pure synthesis that is in good agreement with XRPD, FTIR, and Raman analyses shown and discussed in detail. The elemental weight ratio for Rb and N were found to be 68.52 wt-% and 31.48 wt-%, respectively, from the analysis, which is very close to theoretical values of 67.03 wt-% and 32.97 wt-% expected for RbN_3 , and corroborating the high purity phase obtained by the ion-exchange synthesis.

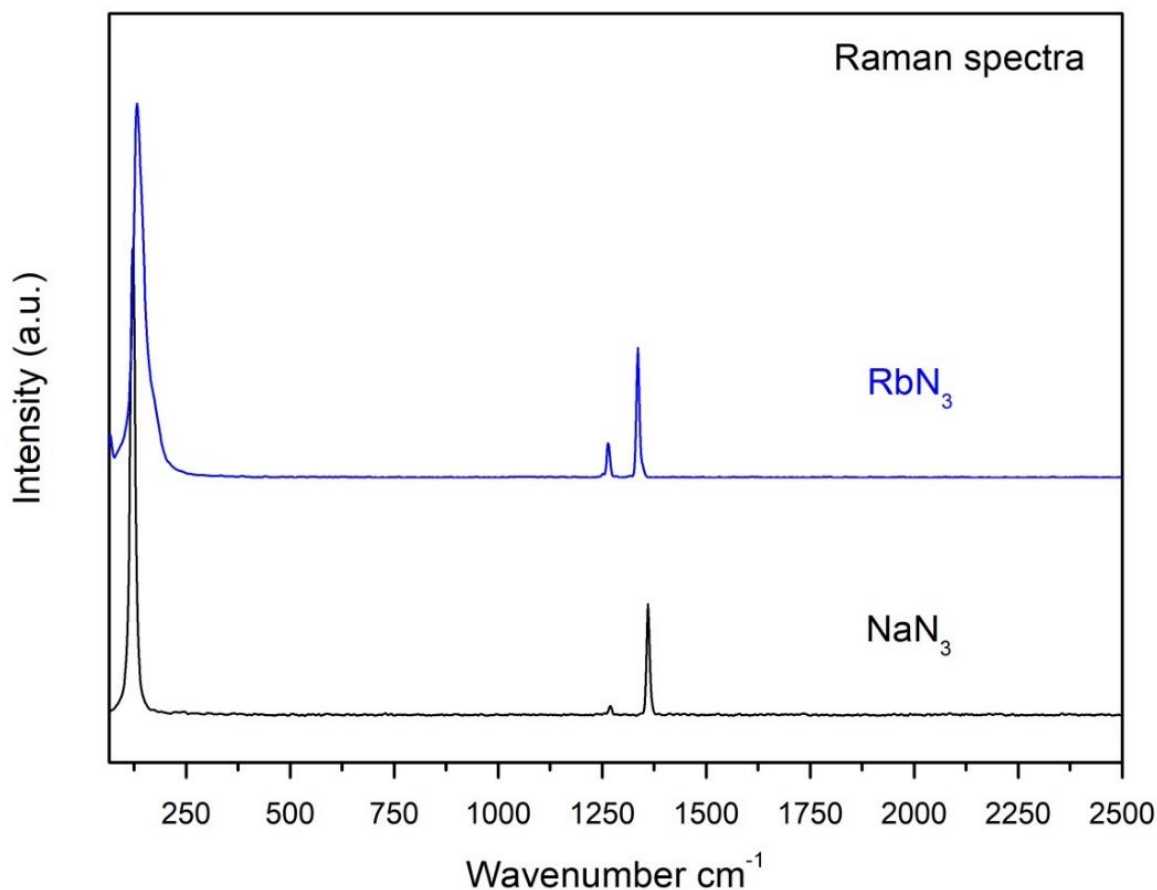


Figure 4: Raman spectrum of the ion-exchange synthesized RbN_3 vs NaN_3 educt.

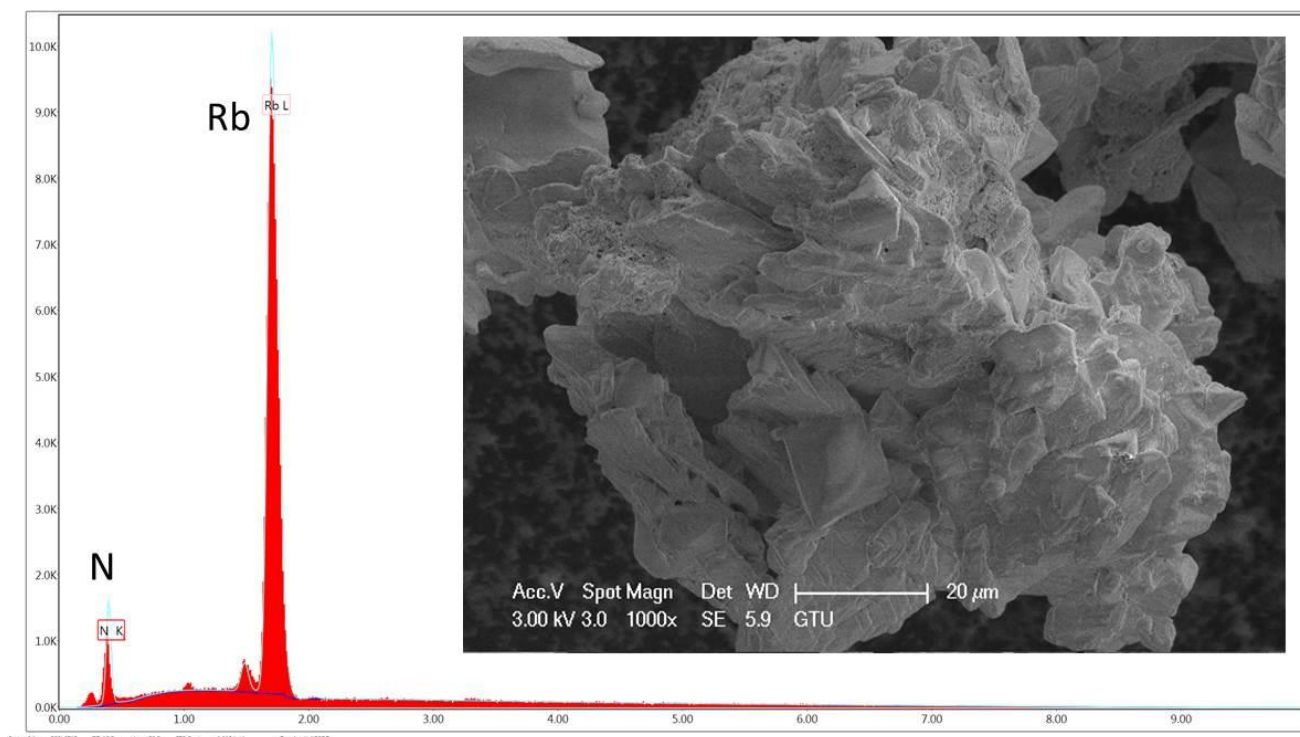


Figure 5: SEM-EDX analysis of the ion-exchange synthesized RbN_3 .

4. CONCLUSION

In conclusion, azides have captivated the interest of researchers for over a century due to their intriguing chemistry and diverse applications, ranging from their use in airbags and detonators to various other fields. Even with the extensive

exploration of azide chemistry in literature, there remains a gap in detailed research on the synthesis and characterization of binary azides. In this study, a robust and safe method for the synthesis of RbN_3 via ion exchange was presented. The meticulous experimental procedure, outlined with utmost safety precautions, yielded high-purity RbN_3 , as confirmed

by X-ray powder diffraction (XRPD), Fourier-transform infrared spectroscopy (FTIR), and Raman spectroscopy analyses. X-ray powder diffraction (XRPD) coupled with the reference intensity ratio (RIR) analysis confirmed a phase purity above $\sim 99\%$. The synthesized RbN_3 exhibited a crystalline white powder morphology confirmed by optical observations and SEM-EDX analysis, devoid of impurities, thus affirming the efficacy of the ion exchange method. Further characterization analyses by vibrational spectroscopy (FTIR and Raman) provided additional insights into the structure and purity of RbN_3 , aligning well with theoretical expectations and confirming the successful synthesis. These findings underscore the importance of developing safe and reliable methods for the synthesis of binary azides and pave the way for future research exploring their potential applications across various fields. Moreover, this study contributes to the broader understanding of azide chemistry, offering valuable insights into the synthesis and characterization of complex azide compounds.

5. CONFLICT OF INTEREST

There is no conflict of interest.

6. ACKNOWLEDGMENTS

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