

# Formation and Crystallization Behavior of a New Organic–Inorganic Hybrid Crystalline Compound in the $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 - \text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} - \text{H}_2\text{O}$ System <sup>†</sup>

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## Abstract

Organic–inorganic hybrid crystalline materials formed in multicomponent aqueous systems are of interest because their phase behavior and physicochemical properties can be controlled by composition and crystallization conditions. In this study, the phase equilibria and crystallization behavior of the ternary aqueous  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 - \text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} - \text{H}_2\text{O}$  system were investigated over the temperature range of  $-24$  to  $60$  °C using the visual-polythermal method. Experimental data obtained for the two boundary binary subsystems and eight internal sections were used to construct the polythermal phase diagram. The diagram revealed distinct crystallization fields corresponding to ice,  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , and a separate crystallization region associated with a previously unreported crystalline phase with the proposed composition  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ . The solid phase was isolated from its crystallization region, washed with cold distilled water, dried to constant mass, and characterized by complementary Fourier-transform infrared spectroscopy (FT-IR), scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS), thermogravimetric analysis, derivative thermogravimetry, and differential scanning calorimetry (TG-DTG-DSC), and powder X-ray diffraction (PXRD). The experimentally determined  $\text{Ca}^{2+}$  and  $\text{ClO}_3^-$  contents were reasonably consistent with the proposed composition, while FT-IR spectroscopy revealed characteristic chlorate vibrations and changes in the vibrational environment of the organic component. SEM showed predominantly prismatic and plate-like crystalline morphologies, and EDS confirmed the presence of Ca, Cl, O, C, and N. Thermal analysis demonstrated multistage decomposition, with comparatively good thermal stability below approximately  $150$  °C. PXRD revealed a diffraction fingerprint distinct from those of the starting components and the corresponding physical mixture. Preliminary indexing of 19 principal reflections was consistent with a tetragonal candidate lattice with  $a = b = 7.7411(5)$  Å,  $c = 24.7182(10)$  Å,  $V = 1481.2(5)$  Å<sup>3</sup>, and  $M_{20} \approx 23.0$ . The crystallographic analysis is considered preliminary because the diffraction profile was reconstructed from the available pattern and was not subjected to complete structure refinement. Overall, the combined phase-equilibrium, compositional, spectroscopic, morphological, thermal,



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and diffraction data support the isolation of a distinct organic–inorganic crystalline phase with the proposed composition.

**Keywords:** organic–inorganic crystalline phase; ternary phase equilibria; polythermal crystallization; calcium chlorate–urea system; triethanolammonium monochloroacetate; FT-IR spectroscopy; SEM-EDS; thermal analysis; powder X-ray diffraction; preliminary crystallographic indexing

## 1. Introduction

Organic–inorganic hybrid crystalline materials have attracted considerable scientific interest because they combine the structural rigidity and thermal stability of inorganic components with the functional versatility of organic molecules. Such hybrid systems often exhibit unique physicochemical properties including tunable solubility, hydrogen-bonding networks, ion conductivity, and controlled crystallization behavior, which make them promising for applications in agrochemistry, pharmaceuticals, catalysis, and functional materials engineering [1–3]. In recent years, the investigation of multicomponent aqueous systems containing inorganic salts and organic ligands has become an important direction in crystal engineering and phase chemistry.

Particular attention has been devoted to hybrid crystals formed through intermolecular interactions between metal-containing inorganic salts and proton-donor organic compounds. Hydrogen bonding, electrostatic interactions, and coordination effects play a decisive role in stabilizing these systems and determining their crystallization pathways [4,5]. According to Desiraju and Steiner, hydrogen-bond organization strongly influences the formation of supramolecular architectures in molecular crystals and controls phase stability in multicomponent systems [6]. In aqueous media, the presence of ionic species further complicates crystallization processes, leading to the formation of hydrates, double salts, or hybrid crystalline compounds with distinct physicochemical properties [7].

Among inorganic oxidizing salts, calcium chlorate systems are of particular interest due to their strong oxidizing ability, high water solubility, and potential agrochemical applications. Chlorate-containing compounds are widely investigated as components of defoliants, herbicides, and energetic materials [8,9]. The crystal chemistry of chlorate salts has been studied extensively because chlorate anions exhibit characteristic coordination behavior and participate actively in hydrogen-bonded crystal networks [10]. Previous investigations demonstrated that chlorate ions are capable of forming stable crystalline phases with amines, amino alcohols, and organic acids through ionic and hydrogen-bond interactions [11].

Organic amino alcohols such as triethanolamine are especially important in hybrid crystal chemistry because they possess both donor hydroxyl groups and a tertiary nitrogen atom capable of protonation. Triethanolamine can therefore participate simultaneously in coordination, hydrogen bonding, and acid–base interactions [12]. Numerous studies have shown that triethanolamine readily forms crystalline complexes with inorganic salts and carboxylic acids, producing supramolecular structures with enhanced thermal and physicochemical stability [13,14]. The hydroxyl groups of triethanolamine contribute to extensive hydrogen-bond networks, while protonation of the nitrogen center promotes ionic interactions within the crystal lattice [15].

Monochloroacetic acid is another important organic component frequently used in the preparation of functional hybrid systems. Owing to the presence of both a reactive chloro substituent and a carboxylic group, monochloroacetic acid can participate in proton-

transfer reactions and form stable salts with amines and amino alcohols [16]. Earlier investigations demonstrated that monochloroacetic acid forms crystalline compounds with ethanolamines and other nitrogen-containing organic bases, where the stabilization of the crystal structure is mainly governed by hydrogen bonding between carboxylate and hydroxyl groups [17]. Such systems are particularly interesting because they may exhibit controlled crystallization behavior and improved physicochemical characteristics relevant to agrochemical formulations.

The formation of hybrid crystals in aqueous multicomponent systems is closely related to phase equilibria and solubility relationships. Therefore, the construction of polythermal solubility diagrams remains one of the most informative approaches for studying complex crystallization processes [18]. The visual-polythermal method is widely used for determining phase boundaries, crystallization fields, eutonic regions, and invariant equilibrium points in ternary and quaternary systems [19]. Polythermal phase diagrams provide valuable information about the temperature and concentration ranges in which individual phases exist and allow the identification of previously unknown crystalline compounds [20].

A number of investigations have demonstrated the effectiveness of polythermal analysis for discovering new hybrid crystalline materials in water–salt–organic systems. For example, Seidell and Linke reported that multicomponent aqueous systems often produce intermediate crystalline phases not predictable solely from binary interactions [21]. More recent studies confirmed that the introduction of organic ligands into inorganic salt solutions can substantially alter crystallization mechanisms and generate new supramolecular architectures [22]. Similar observations were reported for chlorate-containing systems with amino alcohols, where distinct crystallization fields corresponding to new compounds were detected on phase diagrams [23].

Infrared spectroscopy is commonly employed for confirming the formation of hybrid crystalline compounds because vibrational bands are highly sensitive to intermolecular interactions and structural rearrangements [24]. Changes in the stretching vibrations of hydroxyl, amino, chlorate, and carboxylate groups can provide direct evidence of proton transfer, coordination effects, and hydrogen-bond formation within the crystal structure [25]. In hybrid chlorate systems, characteristic bands of the  $\text{ClO}_3^-$  ion usually appear in the  $900\text{--}1000\text{ cm}^{-1}$  region, while carboxylate vibrations and broadened O–H bands reflect the participation of organic components in supramolecular interactions [26].

Despite numerous investigations devoted to organic–inorganic hybrid crystals, information concerning phase equilibria and crystallization behavior in the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2\text{--CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N--H}_2\text{O}$  system remains absent in the literature. In particular, the formation conditions, stability regions, and physicochemical characteristics of hybrid crystalline phases in this system have not been systematically studied. Therefore, investigation of this ternary aqueous system is important both from a theoretical viewpoint and for the development of new multifunctional crystalline materials with possible agrochemical applications.

The present work focuses on the physicochemical investigation of the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2\text{--CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N--H}_2\text{O}$  system over a wide temperature range using the visual-polythermal method. Particular attention was given to the identification of crystallization fields, determination of phase-equilibrium relationships, isolation of the solid phase formed within the corresponding crystallization region, and its physicochemical characterization. The isolated material was investigated by chemical analysis, FT-IR spectroscopy, SEM-EDS, TG-DTG-DSC thermal analysis, and PXRD. The PXRD data were additionally examined by preliminary indexing to obtain crystallographic information on the isolated phase; however, the present study does not claim a complete determination of its atomic crystal structure.

## 2. Experimental

The objects of investigation were calcium dicarbamidochlorate and triethanolammonium monochloroacetate. Calcium dicarbamidochlorate was synthesized by the interaction of molten urea with calcium chlorate at a molar ratio of components 2:1 ( $2\text{CO}(\text{NH}_2)_2:\text{Ca}(\text{ClO}_3)_2$ ) [7,8].

Conventional analytical chemistry methods were employed for quantitative chemical analysis. In particular, the chlorate ion content was determined by volumetric permanganatometric titration [9,10], while calcium was determined using the volumetric complexometric method [11]. The contents of elemental carbon and hydrogen were determined according to the procedure described in [12].

The solubility of the components was studied using the visual-polythermal method [13] with the aid of a TN-6 mercury-in-glass thermometer operating in the temperature range from  $-30$  to  $+60$  °C and a TL-15 mercury-in-glass thermometer with a measurement range from  $-100$  to  $+20$  °C [14].

Calcium dicarbamidochlorate,  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ , was prepared by reacting calcium chlorate with urea in a molar ratio of 1:2. Calcium chlorate was mixed with two equivalents of urea and heated under continuous stirring until complete interaction occurred. After cooling to room temperature, the obtained product was used for the investigation of the binary  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2\text{--H}_2\text{O}$  system.

Triethanolammonium monochloroacetate,  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , was prepared by gradual neutralization of triethanolamine with monochloroacetic acid. Monochloroacetic acid was added portionwise to triethanolamine under continuous stirring until a neutral medium ( $\text{pH} \approx 7$ ) was reached. The resulting salt solution was subsequently employed for the investigation of the binary  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N--H}_2\text{O}$  system.

The phase equilibria in the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2\text{--CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N--H}_2\text{O}$  system were investigated using the visual-polythermal method.

To construct the ternary polythermal phase diagram, a series of internal sections were prepared using solutions containing 20, 40, and 60 wt% of each binary component.

In the first series of experiments, aqueous solutions containing 20, 40, and 60 wt% calcium dicarbamidochlorate were prepared. Various amounts of triethanolammonium monochloroacetate solution were then added to each solution to obtain different overall compositions. Each mixture was cooled under controlled conditions using liquid nitrogen, while the crystallization temperature was determined with a calibrated mercury thermometer by recording the temperature at which the first visible crystals appeared.

In the second series, 20, 40, and 60 wt% solutions of triethanolammonium monochloroacetate were prepared. Different quantities of calcium dicarbamidochlorate were subsequently added to these solutions. The resulting mixtures were again cooled using liquid nitrogen, and the temperatures corresponding to the onset of crystallization were recorded.

Based on the crystallization temperatures obtained for all investigated compositions, the phase boundaries were determined and a complete polythermal phase diagram of the ternary system was constructed manually on millimeter graph paper. The compositions of the invariant points and crystallization regions presented in Table 1 were derived directly from the constructed polythermal diagram.

The FT-IR spectra of the initial components and the investigated compounds were recorded in the frequency range of  $400\text{--}4000\text{ cm}^{-1}$  using a FT-IR SHIMADZU MIRacle10 spectrometer (Shimadzu Scientific Instruments, Columbia, MD, USA) [15–17].

**Table 1.** Binary and ternary invariant points of the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ – $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} \cdot \text{H}_2\text{O}$  system.

| Liquid Phase, wt%                                           |                                                                            |                      | Crystallization<br>Temperature, °C | Solid Phase                                                                                                                                                                                   |
|-------------------------------------------------------------|----------------------------------------------------------------------------|----------------------|------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ | $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ | $\text{H}_2\text{O}$ |                                    |                                                                                                                                                                                               |
| 1                                                           | 2                                                                          | 3                    | 4                                  | 5                                                                                                                                                                                             |
| 46.0                                                        | -                                                                          | 56.0                 | −15.0                              | Ice + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                                                                             |
| 35.5                                                        | 10.8                                                                       | 53.7                 | −22.9                              | Ice + $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$                                                                                                                                     |
| 31.0                                                        | 13.0                                                                       | 56.0                 | −24.0                              | Ice + $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                        |
| 19.5                                                        | 16.0                                                                       | 64.5                 | −18.0                              | Ice + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                                                                              |
| 16.0                                                        | 18.9                                                                       | 65.1                 | −16.0                              | Ice + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                                                                              |
| 15.0                                                        | 20.0                                                                       | 65.0                 | −14.0                              | Ice + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ |
| 9.5                                                         | 36.0                                                                       | 54.5                 | 9.0                                | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 10.8                                                        | 47.3                                                                       | 41.9                 | 21.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 12.2                                                        | 52.5                                                                       | 35.3                 | 25.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 15.3                                                        | 62.0                                                                       | 22.7                 | 37.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 16.9                                                        | 66.6                                                                       | 16.5                 | 37.8                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 18.2                                                        | 70.0                                                                       | 11.8                 | 40.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 19.4                                                        | 72.8                                                                       | 7.8                  | 41.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 21.8                                                        | 78.2                                                                       | 0.0                  | 43.0                               | $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ + $\text{ClCH}_2\text{COOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$       |
| 32.2                                                        | 13.4                                                                       | 54.4                 | −19.0                              | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 33.5                                                        | 14.8                                                                       | 51.7                 | −18.0                              | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 40.6                                                        | 21.5                                                                       | 37.9                 | 1.0                                | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 42.9                                                        | 28.2                                                                       | 28.9                 | 10.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 44.6                                                        | 33.0                                                                       | 22.4                 | 19.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 46.6                                                        | 42.3                                                                       | 11.1                 | 33.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 47.0                                                        | 47.7                                                                       | 5.3                  | 38.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 46.9                                                        | 53.1                                                                       | 0.0                  | 52.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$                              |
| 60.0                                                        | -                                                                          | 40.0                 | 24.0                               | Ice + $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$                                                                                                                                     |
| 60.2                                                        | 7.9                                                                        | 31.9                 | 31.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |
| 59.9                                                        | 16.0                                                                       | 24.1                 | 38.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |
| 59.2                                                        | 22.5                                                                       | 18.3                 | 44.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |
| 57.5                                                        | 33.8                                                                       | 8.7                  | 52.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |
| 55.5                                                        | 40.0                                                                       | 4.5                  | 57.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |
| 53.2                                                        | 46.7                                                                       | 0.1                  | 60.0                               | $\text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$ + $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$                                                                             |

Powder X-ray diffraction (PXRD) analysis was used to evaluate the crystallinity, phase distinction, and preliminary crystallographic characteristics of the isolated solid phase.

The diffraction patterns of  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ ,  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , and the isolated crystalline phase were compared over the  $2\theta$  range of  $10\text{--}80^\circ$ . The principal reflections of the isolated phase were identified from the displayed diffraction pattern, and the corresponding d-spacings were calculated using Bragg's law with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Nineteen principal reflections were subsequently subjected to preliminary indexing. The indexing procedure yielded a candidate tetragonal unit cell with  $a = b = 7.7411(5) \text{ \AA}$ ,  $c = 24.7182(10) \text{ \AA}$ , and  $V = 1481.2(5) \text{ \AA}^3$ , with an  $M_{20}$  figure of merit of approximately 23.0. Reflection conditions were examined to evaluate possible tetragonal symmetry, and  $P4/mmm$  (No. 123) was considered as a candidate space group. Because the available diffraction profile was reconstructed from the displayed pattern rather than obtained from the original raw instrumental file, the indexing and symmetry assignment are regarded as preliminary. Accordingly, the PXRD analysis is used to provide evidence for phase distinction and a preliminary crystallographic description rather than a complete atomic-structure determination.

The solid phase corresponding to the crystallization region assigned to the proposed hybrid phase was isolated from the polythermal experiments at compositions located within the corresponding crystallization field. After crystallization, the solid material was separated from the mother liquor by filtration. The isolated crystals were carefully washed with a small amount of cold distilled water to remove adhering mother-liquor components while minimizing dissolution of the crystalline phase. The washed material was then dried at room temperature to constant mass. The resulting solid was collected as a crystalline powder and used for chemical analysis, FT-IR, SEM-EDS, TG-DTG-DSC, and PXRD characterization. No single crystal suitable for single-crystal X-ray diffraction was obtained under the experimental conditions employed.

### 3. Results and Discussion

#### 3.1. Phase Equilibria of the Binary Subsystems

The phase-equilibrium behavior of the binary subsystem  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} - \text{H}_2\text{O}$ , which represents one of the boundary subsystems of the investigated ternary system, was first examined. The corresponding polythermal diagram is characterized by crystallization branches of the solid components that converge at a cryohydric point. The cryohydric composition was determined to be approximately 31.8 wt%  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  and 68.2 wt%  $\text{H}_2\text{O}$  at  $-5.8^\circ\text{C}$ . These data define the limiting crystallization behavior of the triethanolammonium monochloroacetate–water subsystem.

The second binary subsystem,  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 - \text{H}_2\text{O}$ , exhibits crystallization regions associated with ice and the calcium dicarbamidochlorate-containing phase. A transition point was observed at approximately  $-15^\circ\text{C}$ , at which the concentration of  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$  was approximately 46.1 wt%. The obtained binary phase-equilibrium data were subsequently used as boundary conditions for the construction and interpretation of the ternary system.

The agreement of the experimental binary-system behavior with previously reported data [18–20] provides a basis for using these subsystems for the subsequent construction of the ternary polythermal phase diagram.

#### 3.2. Phase Equilibria and Crystallization Behavior of the Ternary System

The phase equilibria of the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 - \text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} - \text{H}_2\text{O}$  ternary system were investigated using eight internal sections. The selected compositions included 20, 40, and 60 wt% solutions of the binary components, while the concentration of the second component was varied systematically. The crystallization temperatures obtained for the investigated compositions were used to construct the complete polythermal phase

diagram of the ternary system over the temperature interval from  $-24.0$  to  $60.0$  °C (Figure 1).

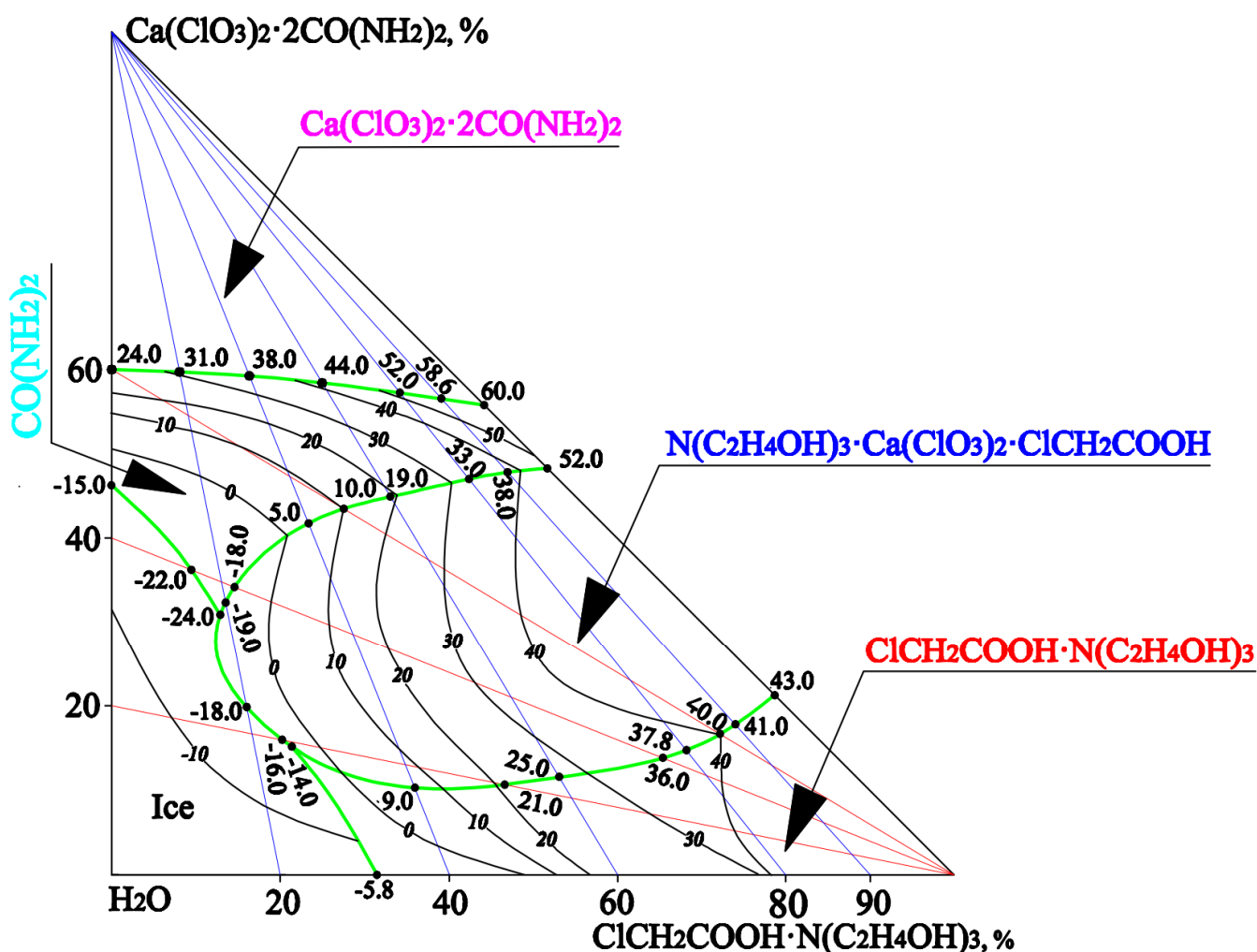


**Figure 1.** Polythermal phase diagram of the  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ – $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ – $\text{H}_2\text{O}$  system.

The resulting phase diagram demonstrates several distinct crystallization regions. These include the crystallization fields of ice,  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , and a separate crystallization region corresponding to the isolated phase with the proposed composition  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ .

The crystallization regions are separated by phase-boundary curves whose intersections define invariant equilibrium points. The compositions of the liquid phases and the corresponding crystallization temperatures are summarized in Table 1.

The polythermal diagram also contains solubility isotherms at  $-20$ ,  $-10$ ,  $0$ ,  $10$ ,  $20$ ,  $30$ , and  $40$  °C. These isotherms provide a visual representation of the dependence of the phase-equilibrium relationships on both temperature and solution composition.

Of particular importance is the crystallization region assigned to  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ . This region is spatially distinguishable from the crystallization fields of the initial binary components. Therefore, the phase-equilibrium study provided an experimental basis for selecting compositions from which the corresponding solid material could be isolated for subsequent characterization.

The phase diagram itself describes the equilibrium relationships within the multicomponent aqueous system, whereas the chemical, spectroscopic, microscopic, thermal, and PXRD investigations described below were performed on the solid material isolated from

the crystallization region assigned to the proposed phase. Consequently, the characterization results are not interpreted as measurements of the multiphase equilibrium mixtures represented by the complete set of compositions in Table 1.

### 3.3. Isolation and Chemical Composition of the Crystalline Phase

The solid phase corresponding to the crystallization region assigned to the proposed phase was isolated from the polythermal experiments. After crystallization, the solid material was separated from the mother liquor by filtration. The isolated material was carefully washed with a small amount of cold distilled water to remove adhering mother-liquor components while minimizing dissolution of the crystalline material. The washed solid was subsequently dried at room temperature to constant mass.

The isolated material was obtained as a crystalline powder. No single crystal of sufficient quality for single-crystal X-ray diffraction was obtained under the experimental conditions employed. Therefore, the structural characterization was performed using powder-based and complementary physicochemical methods.

The chemical composition of the isolated material was compared with the calculated composition of the proposed phase  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ . The experimentally determined contents were 9.11 wt%  $\text{Ca}^{2+}$ , 35.30 wt%  $\text{ClO}_3^-$ , and 3.81 wt% N, whereas the corresponding calculated values were 8.87, 37.06, and 3.10 wt%, respectively.

The deviations between experimental and calculated values were approximately +0.24 wt% for  $\text{Ca}^{2+}$ , −1.76 wt% for  $\text{ClO}_3^-$ , and +0.71 wt% for N. In relative terms, these correspond to deviations of approximately 2.7%, 4.8%, and 22.9%, respectively.

The calcium and chlorate contents show relatively close agreement with the calculated values, whereas the nitrogen content exhibits a larger relative deviation. The deviations may arise from experimental uncertainty, residual mother liquor, minor compositional heterogeneity, incomplete removal of adhering solution, or analytical uncertainty. Therefore, the chemical analysis is considered supporting compositional evidence rather than definitive proof of an exact stoichiometric crystal structure.

Nevertheless, the simultaneous detection of Ca, chlorate-containing species, and nitrogen-containing organic constituents is consistent with the proposed composition of the isolated phase. These results, together with the phase-equilibrium and subsequent spectroscopic, morphological, thermal, and diffraction data, provide cumulative evidence for the formation and isolation of a distinct crystalline phase.

### 3.4. FT-IR Spectroscopic Characterization

FT-IR spectroscopy was used to investigate the vibrational characteristics of the starting triethanolammonium monochloroacetate component and the isolated crystalline phase (Figure 2).

The FT-IR spectrum of  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  contains a broad absorption region between approximately 3415 and 3285  $\text{cm}^{-1}$ , which is associated primarily with O–H stretching vibrations and hydrogen-bonding interactions. The bands at approximately 2938 and 2863  $\text{cm}^{-1}$  can be assigned to asymmetric and symmetric C–H stretching vibrations of methylene groups.

The absorption features observed near 1645, 1075, and 1040  $\text{cm}^{-1}$  can be associated with O–H deformation and C–N/C–O stretching vibrations, respectively. Additional bands in the 1150–980  $\text{cm}^{-1}$  region are consistent with vibrations involving C–O and C–C bonds, while the band near 550  $\text{cm}^{-1}$  is attributable to C–Cl-related vibrational modes.

Changes in the FT-IR spectrum are observed after formation of the isolated phase. In particular, prominent absorption bands near 974 and 914  $\text{cm}^{-1}$  are observed in the

spectrum of the isolated material. These bands are assigned to characteristic stretching vibrations of the chlorate ion.

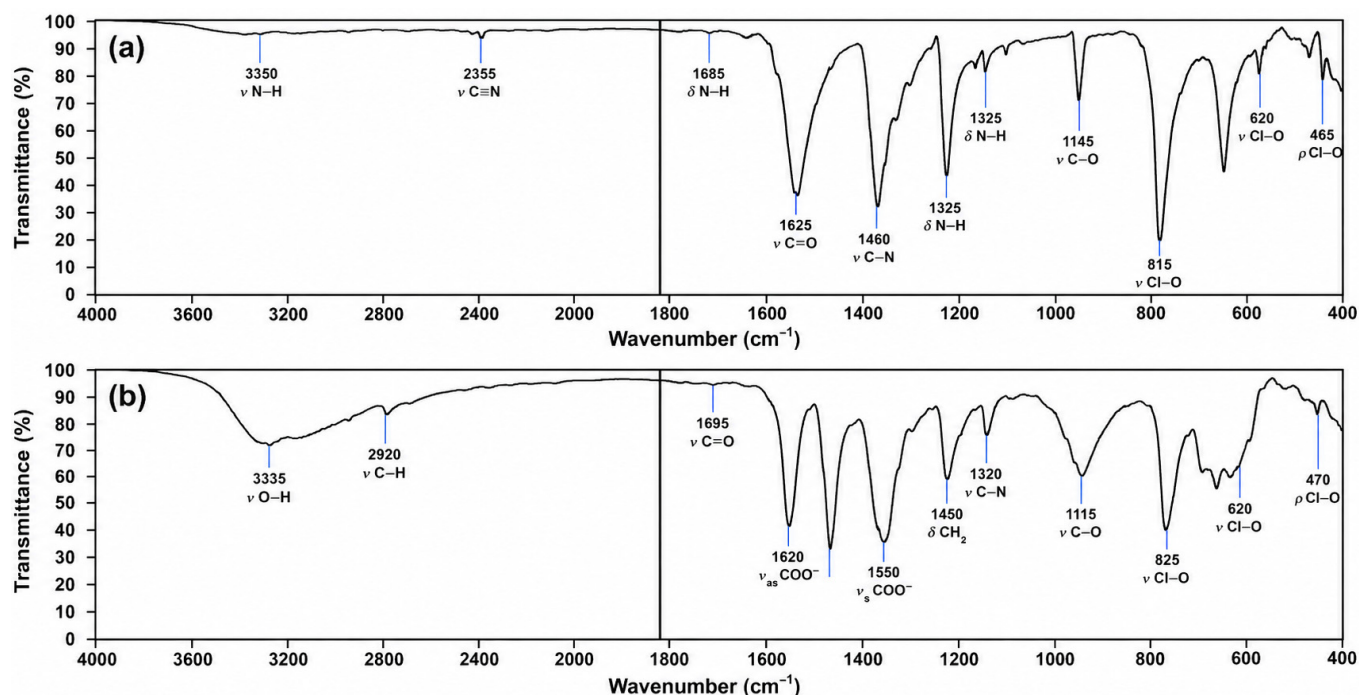


**Figure 2.** FT-IR spectra of (a)  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  and (b) the isolated crystalline phase  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  recorded in the  $400\text{--}4000\text{cm}^{-1}$  spectral range. Selected characteristic absorption bands are indicated.

The appearance of the characteristic chlorate bands provides spectroscopic evidence that chlorate-containing species are present in the isolated material. Changes in the hydroxyl, carboxylate, C–O, and C–N vibrational regions further indicate that the molecular and ionic environment of the organic component differs from that of the starting material.

However, these spectral changes should not be interpreted as direct proof of a particular atomic arrangement or crystallographic symmetry. FT-IR spectroscopy provides information about the molecular and ionic vibrational environment but does not independently establish the crystal system, space group, or atomic coordinates.

Thus, the FT-IR results are considered complementary spectroscopic evidence supporting the proposed composition and phase assignment.

### 3.5. SEM–EDS Characterization

The morphology and elemental composition of the isolated crystalline phase were investigated by scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM–EDS).

The SEM micrographs reveal predominantly well-developed prismatic and plate-like particles with relatively smooth surfaces and distinct crystal boundaries. The particles exhibit a well-developed crystalline morphology, with some surfaces showing narrow growth terraces and layered features.

These observations describe the morphology of the isolated solid. In accordance with the reviewer’s recommendation, SEM is not used to establish the nucleation mechanism, homogeneous nucleation, crystal-system symmetry, space group, or atomic structure (Figure 3).

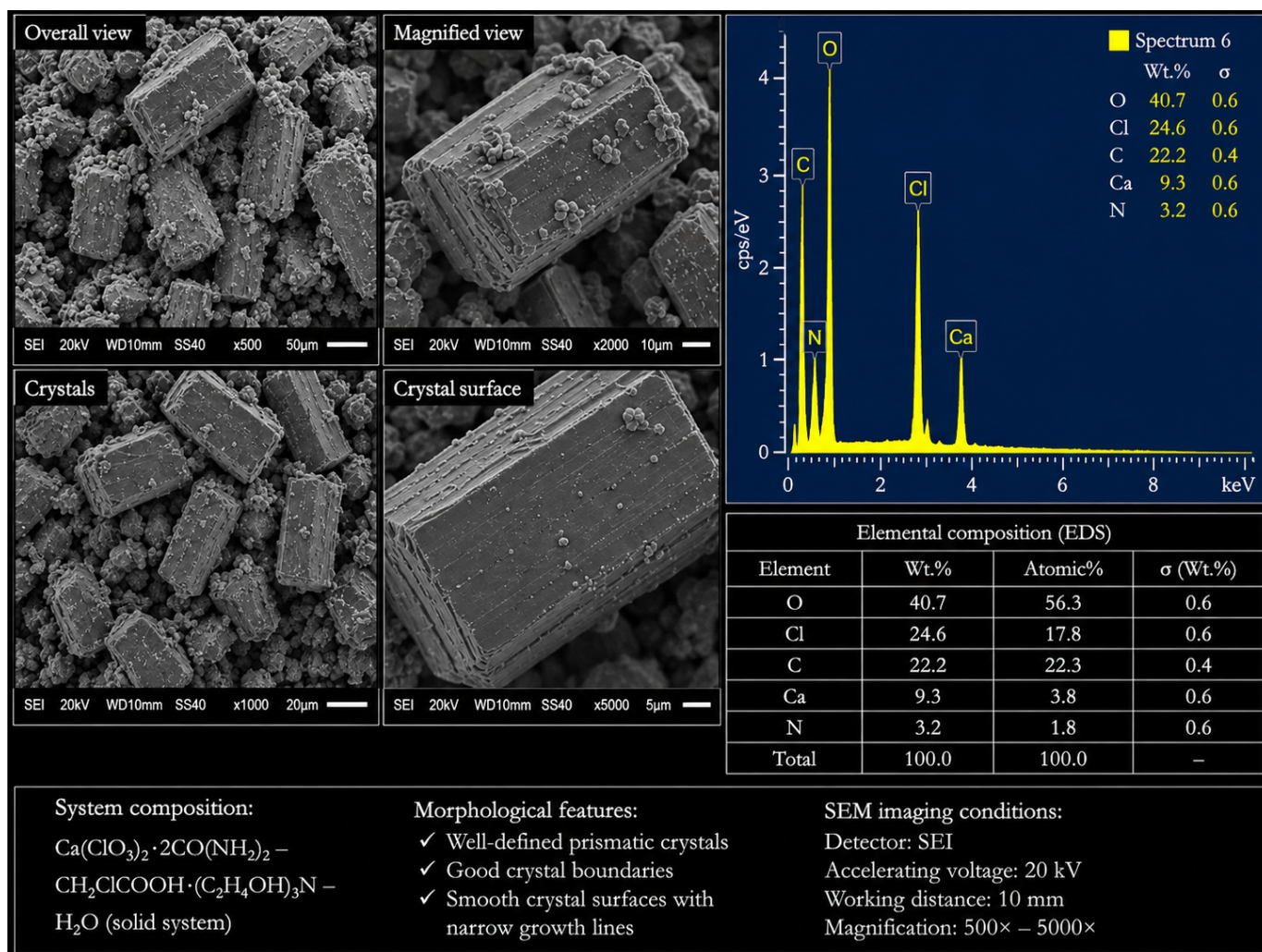


**Figure 3.** SEM micrographs of the isolated  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  crystalline phase at different magnifications.

The EDS spectrum shows signals corresponding to Ca, Cl, O, C, and N, which are the principal elements expected from the proposed organic–inorganic composition. The simultaneous presence of calcium and chlorine is consistent with the chlorate-containing inorganic component, while carbon, oxygen, and nitrogen are consistent with the organic constituents.

The EDS results therefore provide complementary elemental evidence for the proposed composition. However, EDS cannot establish molecular connectivity, ionic arrangement, or crystallographic symmetry.

Accordingly, the SEM–EDS results are interpreted exclusively in terms of morphology and elemental composition. They support, but do not independently establish, the assignment of the isolated material as a distinct crystalline phase.

### 3.6. TG–DTG–DSC Thermal Behavior

The thermal behavior of the isolated crystalline phase  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  was investigated by simultaneous TG–DTG–DSC analysis (Figure 4).

The thermal curves demonstrate a multistage decomposition process accompanied by successive mass losses and endothermic/exothermic thermal effects.

The first stage occurs approximately between 25 and 120 °C and is characterized by a mass loss of approximately 10.2%. A weak endothermic effect centered near 88 °C is

observed on the DSC curve. This initial mass loss is attributed primarily to the removal of physically adsorbed moisture and weakly retained volatile species. Because the proposed isolated-phase composition does not contain a stoichiometric water molecule, this stage is not interpreted as definitive evidence for lattice water.

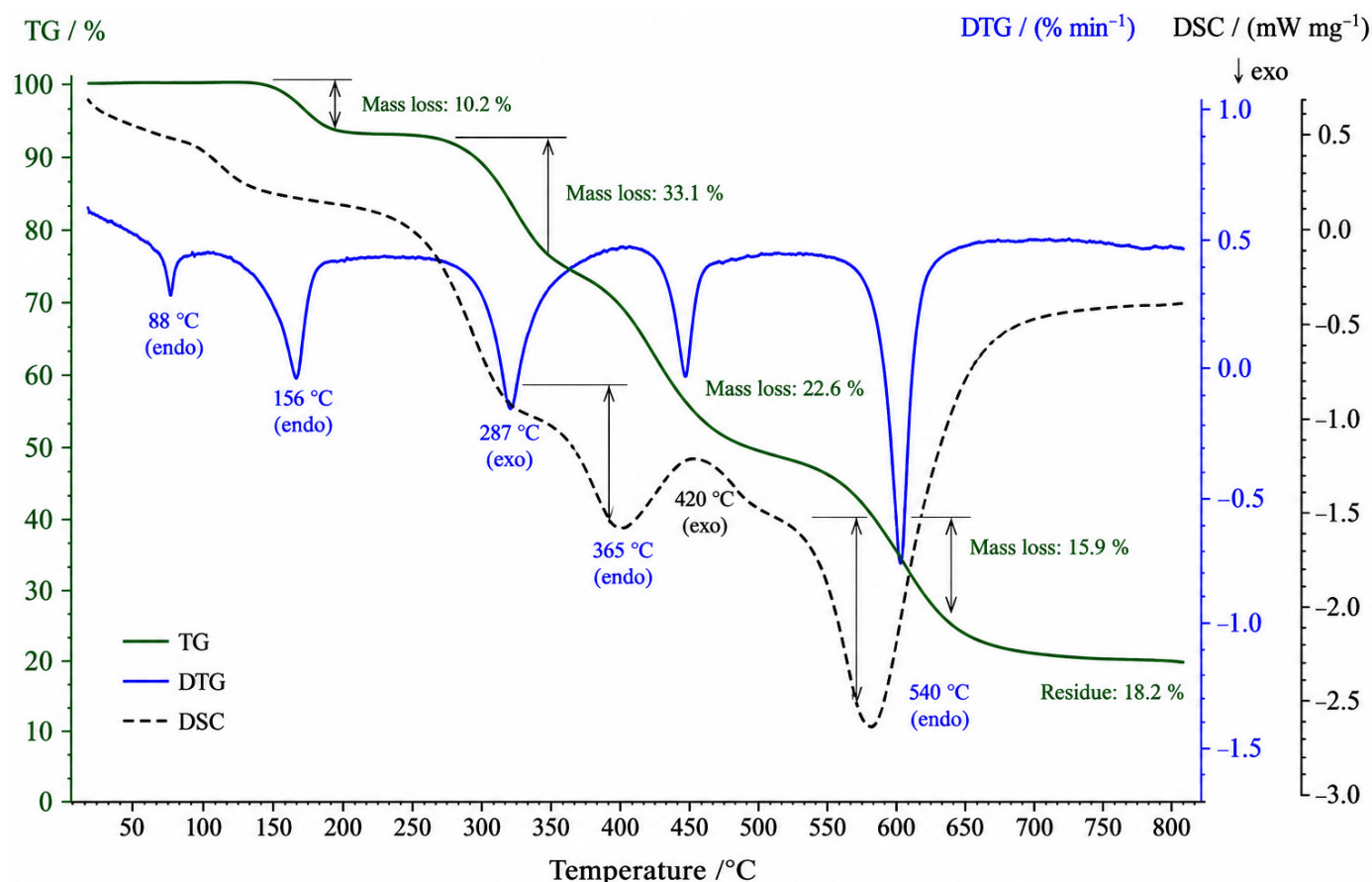


**Figure 4.** TG–DTG–DSC curves of the isolated  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  crystalline phase. The arrows and horizontal guide lines indicate the temperature intervals used to estimate the corresponding mass-loss steps from the TG curve.

The second stage occurs approximately between 120 and 250 °C and corresponds to a larger mass loss of approximately 33.1%. The DTG curve exhibits a pronounced minimum near 156 °C, accompanied by an endothermic effect in the DSC curve.

This stage is attributed primarily to progressive degradation of the organic constituents of the isolated phase, particularly the triethanolamine- and monochloroacetate-derived components. The process is not assigned to urea decomposition because urea is not included in the proposed composition of the isolated crystalline phase.

Further heating between approximately 250 and 400 °C produces an additional mass loss of approximately 22.6%. This process is accompanied by a thermal effect near 287 °C and a broad DSC feature centered around 365 °C. The observed behavior is consistent with further degradation of the organic framework and decomposition of the monochloroacetate-derived component.

A fourth decomposition stage occurs approximately between 400 and 600 °C and is associated with a mass loss of approximately 15.9%. A pronounced thermal effect near 540 °C is observed. This stage is attributed primarily to thermal transformation and decomposition of the chlorate-containing inorganic fraction.

Above approximately 600 °C, the TG curve approaches a relatively stable plateau. The residual mass at approximately 800 °C is about 18.2% of the initial sample mass. The exact

phase composition of this final residue cannot be established solely from TG–DTG–DSC analysis and would require independent characterization of the residue.

Overall, the thermal profile indicates comparatively good thermal stability of the isolated material below approximately 150 °C, followed by progressive decomposition at higher temperatures. The TG–DTG–DSC data provide information on thermal stability and decomposition behavior and are interpreted as complementary evidence rather than as direct evidence of crystallographic structure.

### 3.7. PXRD Characterization and Preliminary Crystallographic Indexing

Powder X-ray diffraction was used to evaluate the crystallinity and phase distinction of the isolated material.

The PXRD pattern of the isolated phase differs from those of the individual starting components and from the physical-mixture/reference pattern. The isolated material exhibits a characteristic sequence of diffraction reflections, with prominent peaks at approximately  $2\theta = 21.50^\circ$ ,  $25.50^\circ$ ,  $29.80^\circ$ ,  $32.90^\circ$ , and  $33.70^\circ$  (Figure 5).

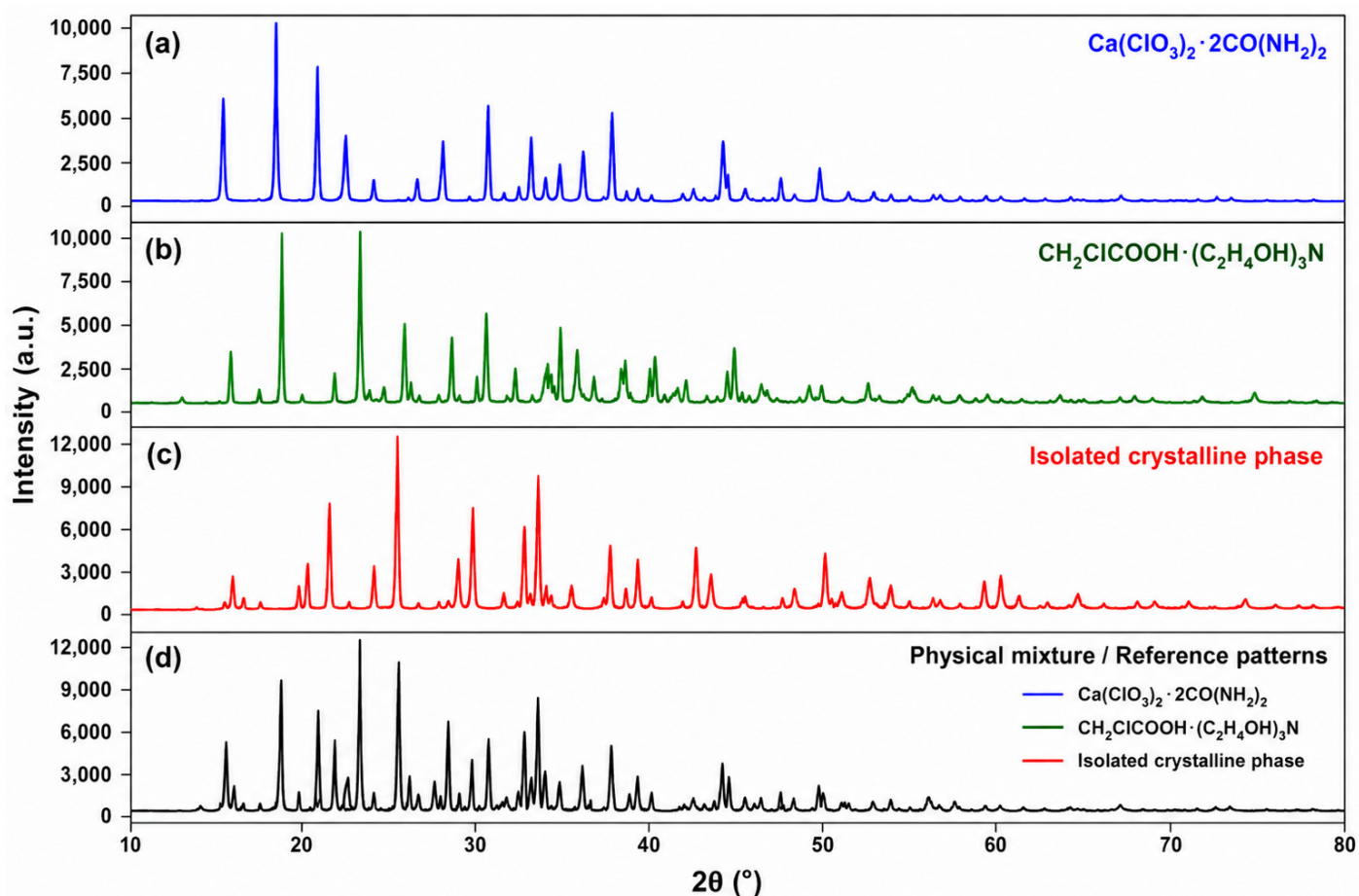


**Figure 5.** PXRD patterns of the starting components and the isolated crystalline phase: (a)  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2$ , (b)  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , (c) isolated crystalline phase, and (d) physical-mixture/reference pattern. The isolated material exhibits a diffraction fingerprint distinguishable from those of the starting components and the corresponding physical-mixture/reference pattern.

The most intense reflection occurs at approximately  $2\theta = 25.50^\circ$ , corresponding to  $\text{\AA}$ . Other prominent reflections occur at  $21.50^\circ$  ( $\text{\AA}$ ),  $29.80^\circ$  ( $\text{\AA}$ ),  $32.90^\circ$  ( $\text{\AA}$ ), and  $33.70^\circ$  ( $\text{\AA}$ ) (Table 2).

**Table 2.** Principal PXRD reflections and preliminary indexing of the isolated crystalline phase.

| No. | 2 $\theta_{\text{obs}}$ (°) | d <sub>obs</sub> (Å) | hkl    | 2 $\theta_{\text{calc}}$ (°) | d <sub>calc</sub> (Å) | $\Delta 2\theta$ (°) |
|-----|-----------------------------|----------------------|--------|------------------------------|-----------------------|----------------------|
| 1   | 15.70                       | 5.6399               | (013)  | 15.6949                      | 5.6417                | +0.0051              |
| 2   | 19.70                       | 4.5029               | (113)  | 19.4535                      | 4.5593                | +0.2465              |
| 3   | 21.50                       | 4.1298               | (006)  | 21.5531                      | 4.1197                | −0.0531              |
| 4   | 23.90                       | 3.7202               | (022)  | 24.0744                      | 3.6937                | −0.1744              |
| 5   | 25.50                       | 3.4903               | (023)  | 25.4041                      | 3.5033                | +0.0959              |
| 6   | 28.80                       | 3.0974               | (008)  | 28.8729                      | 3.0898                | −0.0729              |
| 7   | 29.80                       | 2.9957               | (124)  | 29.5524                      | 3.0203                | +0.2476              |
| 8   | 32.90                       | 2.7202               | (221)  | 32.8991                      | 2.7203                | +0.0009              |
| 9   | 33.70                       | 2.6574               | (126)  | 33.7923                      | 2.6504                | −0.0923              |
| 10  | 35.80                       | 2.5062               | (224)  | 35.8557                      | 2.5024                | −0.0557              |
| 11  | 37.80                       | 2.3781               | (034)  | 37.7499                      | 2.3811                | +0.0501              |
| 12  | 39.48                       | 2.2807               | (226)  | 39.4979                      | 2.2797                | −0.0179              |
| 13  | 42.70                       | 2.1158               | (232)  | 42.7110                      | 2.1153                | −0.0110              |
| 14  | 43.50                       | 2.0788               | (1111) | 43.5000                      | 2.0788                | +0.00002             |
| 15  | 50.20                       | 1.8159               | (0212) | 50.1265                      | 1.8184                | +0.0735              |
| 16  | 52.70                       | 1.7355               | (2211) | 52.6593                      | 1.7367                | +0.0407              |
| 17  | 54.00                       | 1.6967               | (047)  | 53.9869                      | 1.6971                | +0.0131              |
| 18  | 59.50                       | 1.5523               | (2311) | 59.5002                      | 1.5523                | −0.0002              |
| 19  | 60.40                       | 1.5314               | (0313) | 60.4279                      | 1.5307                | −0.0279              |

Note: The d-spacings were calculated using Bragg's law with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å). The hkl assignments represent a preliminary indexing solution for the selected principal reflections.

The characteristic sequence of reflections differs from those of the starting materials, providing evidence that the isolated material is not represented simply by the superposition of the diffraction fingerprints of the initial components.

Preliminary indexing: In addition to qualitative phase comparison, the principal reflections of the isolated phase were subjected to preliminary indexing. Nineteen reflections were indexed using the candidate tetragonal lattice.

The indexing yielded a tetragonal candidate lattice with  $a = b = 7.7411(5)$  Å,  $c = 24.7182(10)$  Å, and  $V = 1481.2(5)$  Å<sup>3</sup>.

The calculated indexing figure of merit is approximately:  $M_{20} = 23.0$ .

The obtained unit-cell parameters and indexing information are summarized in Table 3.

**Table 3.** Preliminary crystallographic parameters obtained from PXRD indexing of the isolated crystalline phase.

| Parameter                     | Value            |
|-------------------------------|------------------|
| Crystal system                | Tetragonal       |
| Lattice centering             | Primitive, P     |
| Space group                   | P4/mmm (No. 123) |
| a (Å)                         | 7.7411(5)        |
| b (Å)                         | 7.7411(5)        |
| c (Å)                         | 24.7182(10)      |
| $\alpha$ (°)                  | 90               |
| $\beta$ (°)                   | 90               |
| $\gamma$ (°)                  | 90               |
| V (Å <sup>3</sup> )           | 1481.2(5)        |
| $M_{20}$                      | 23.0             |
| Number of indexed reflections | 19               |

### 3.7.1. Assessment of the Candidate Tetragonal Lattice

The correspondence between the observed and calculated peak positions provides a preliminary assessment of the proposed tetragonal unit cell (Figure 6). For the 19 indexed reflections, the calculated peak positions generally reproduce the observed peak sequence, although several reflections show measurable deviations. The average absolute deviation in  $2\theta$  is approximately  $0.067^\circ$ , while the largest individual deviation is approximately  $0.248^\circ$ .

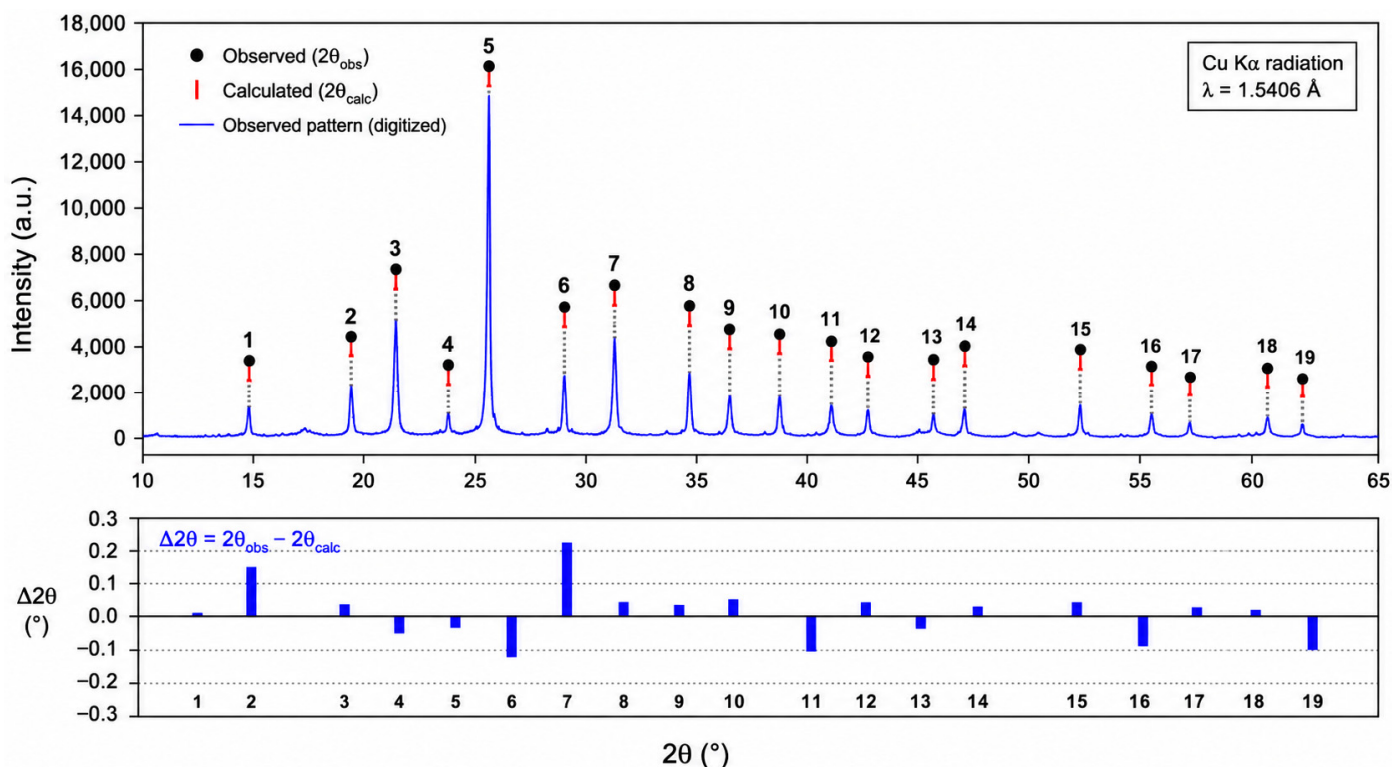


**Figure 6.** Comparison of observed and calculated PXRD peak positions for the preliminary primitive-tetragonal indexing of the isolated crystalline phase. The calculated positions are based on the candidate unit cell  $a = b = 7.7411(5) \text{ \AA}$  and  $c = 24.7182(10) \text{ \AA}$ .

The indexed reflections are compatible with a primitive tetragonal metric lattice characterized by  $a = b = 7.7411(5) \text{ \AA}$ ,  $c = 24.7182(10) \text{ \AA}$ , and  $V = 1481.2(5) \text{ \AA}^3$ . The  $M_{20}$  figure of merit of approximately 23.0 indicates that the proposed indexing provides a reasonably consistent solution for the selected reflections (Table 4).

Reflection-condition analysis further indicates that an I-centered tetragonal lattice is inconsistent with the present indexing because several observed reflections possess odd values of  $h + k + l$ . The observed 00L reflections also provide constraints on possible screw-axis models. Nevertheless, the available peak-position information does not uniquely distinguish all primitive tetragonal space groups. Therefore,  $P4/mmm$  (No. 123) is retained only as a candidate space group for profile testing and not as a definitive assignment.

Consequently, the crystallographic information obtained in this study should be described as a preliminary tetragonal crystallographic model. It establishes the unit-cell metrics and provides constraints on lattice centering and possible symmetry, but it does not constitute a complete structure solution.

**Table 4.** Reflection-condition assessment for the preliminary tetragonal indexing.

| Observation                                   | Indexed Reflection(s)                          | Crystallographic Implication                                                                                       |
|-----------------------------------------------|------------------------------------------------|--------------------------------------------------------------------------------------------------------------------|
| 00L reflections observed with $l = 6$ and $8$ | (006), (008)                                   | Compatible with a primitive tetragonal lattice; excludes tetragonal $4_1/4_3$ screw-axis models requiring $l = 4n$ |
| Reflections with $h + k + l$ odd are observed | (113), (023), (126)                            | Inconsistent with I-centering under the proposed indexing                                                          |
| General hkl reflections observed              | (013), (113), (124), (221), (226), etc.        | No evidence for a unique glide/screw extinction scheme                                                             |
| Overall metric symmetry                       | $a = b$ ; $\alpha = \beta = \gamma = 90^\circ$ | Consistent with tetragonal crystal system                                                                          |
| Unique space group                            | Not established                                | Peak positions alone are insufficient to distinguish all primitive tetragonal candidates                           |

### 3.7.2. Profile Analysis and Limitations of the Crystallographic Interpretation

A preliminary Le Bail-type profile analysis was performed to evaluate the consistency of the candidate tetragonal cell with the available diffraction profile. The obtained residual values were  $R_p = 74.89\%$ ,  $R_{wp} = 51.45\%$ ,  $R_{exp} = 4.27\%$ , and  $\chi^2 = 145.15$  (GoF = 12.05).

The relatively high residual values indicate that the profile agreement is not sufficient to regard the analysis as a final crystallographic refinement. This limitation is attributed primarily to the fact that the available diffraction profile was reconstructed from the displayed PXRD pattern rather than obtained from the original raw instrumental dataset, and therefore instrumental peak widths, background treatment, counting statistics, and experimental uncertainties were not available.

The Le Bail-type analysis is consequently used only as a profile-consistency test of the candidate unit cell, rather than as evidence for a refined crystal structure or a definitive space-group assignment. In particular, the analysis does not provide atomic coordinates, site occupancies, bond distances, or bond angles.

### 3.7.3. Integration of PXRD with Complementary Characterization

The PXRD results provide crystallographic information that is complementary to the other characterization techniques used in this study.

Chemical analysis provides information on the bulk elemental/ionic composition. FT-IR spectroscopy provides information on the molecular and ionic vibrational environment. SEM-EDS provides information on crystal morphology and elemental composition. TG-DTG-DSC characterizes the thermal stability and decomposition behavior. PXRD provides information on the crystalline nature, diffraction fingerprint, and preliminary lattice parameters.

These methods therefore address different structural levels and should not be interpreted as interchangeable evidence.

Importantly, the PXRD-derived crystallographic information is not used to retroactively assign crystallographic meaning to the SEM, EDS, or FT-IR observations. Instead, each technique is interpreted according to its own information content. The PXRD analysis establishes a distinct diffraction pattern and provides a preliminary tetragonal unit-cell description, whereas chemical analysis, FT-IR, SEM-EDS, and TG-DTG-DSC independently characterize composition, vibrational environment, morphology/elemental composition, and thermal behavior, respectively. The agreement among these independent observations

supports phase assignment at the material-characterization level but does not substitute for a complete crystallographic structure determination.

Taken together, the different characterization results provide mutually supportive evidence for the formation and isolation of a distinct crystalline phase with the proposed composition  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ .

### 3.8. Overall Interpretation of the Isolated Phase

The phase-equilibrium study demonstrated a separate crystallization region within the ternary system, providing the basis for isolation of the corresponding solid material. The chemical composition of the isolated material was broadly compatible with the proposed  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$  composition.

The FT-IR spectrum revealed characteristic chlorate vibrations at approximately 974 and 914  $\text{cm}^{-1}$  and changes in the vibrational environment of the organic constituents. SEM-EDS demonstrated well-developed prismatic and plate-like crystal morphology and detected Ca, Cl, O, C, and N. The thermal analysis showed multistage decomposition and comparatively good stability below approximately 150 °C.

PXRD independently demonstrated a diffraction pattern distinguishable from those of the starting materials and physical mixture. Preliminary indexing of 19 principal reflections yielded a tetragonal candidate lattice with  $a = b = 7.7411(5) \text{ \AA}$ ,  $c = 24.7182(10) \text{ \AA}$ , and  $V = 1481.2(5) \text{ \AA}^3$ , with  $M_{20} \approx 23.0$ .

Thus, the different analytical methods provide complementary rather than redundant evidence for the isolated phase. The phase-equilibrium data establish its crystallization field, chemical analysis supports its composition, FT-IR characterizes its vibrational environment, SEM-EDS describes morphology and elemental composition, TG-DTG-DSC describes thermal behavior, and PXRD provides preliminary crystallographic information.

The isolated material is therefore described as a distinct organic-inorganic crystalline phase with the proposed composition, rather than as a fully structurally solved new compound.

A definitive determination of the space group, atomic coordinates, interatomic distances, and three-dimensional crystal structure would require a complete experimental diffraction dataset suitable for full profile refinement and, preferably, single-crystal X-ray diffraction.

## 4. Conclusions

The phase equilibria and crystallization behavior of the ternary aqueous  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 - \text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N} - \text{H}_2\text{O}$  system were systematically investigated over the temperature range from  $-24$  to  $60 \text{ }^\circ\text{C}$  using the visual-polythermal method. The binary boundary subsystems and eight internal sections were used to construct the polythermal phase diagram, which revealed distinct crystallization fields for ice,  $\text{Ca}(\text{ClO}_3)_2 \cdot 2\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{CH}_2\text{ClCOOH} \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ , and a separate crystalline phase with the proposed composition  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ .

The solid phase corresponding to this crystallization region was isolated from the mother liquor, washed with cold distilled water, dried to constant mass, and obtained as a crystalline powder. Chemical analysis gave 9.11 wt%  $\text{Ca}^{2+}$ , 35.30 wt%  $\text{ClO}_3^-$ , and 3.81 wt% N, which provides compositional support for the proposed hybrid phase, although the relatively larger deviation in the nitrogen content indicates that the analytical results should not be regarded as definitive proof of exact stoichiometry.

FT-IR spectroscopy revealed characteristic chlorate vibrations together with changes in the vibrational regions associated with the organic component. SEM demonstrated predominantly prismatic and plate-like crystal morphologies, while EDS confirmed the presence of Ca, Cl, O, C, and N. In accordance with the limitations of these techniques,

SEM–EDS was used to describe morphology and elemental composition and was not used to infer nucleation mechanism, crystallographic symmetry, or atomic structure. TG–DTG–DSC analysis demonstrated multistage thermal decomposition, beginning with the loss of weakly retained moisture and followed by degradation of the organic constituents and thermal transformation of the chlorate-containing fraction. The isolated material exhibited comparatively good thermal stability below approximately 150 °C.

PXRD analysis provided additional evidence for the crystalline nature and phase distinction of the isolated material. The diffraction pattern of the isolated phase was distinguishable from those of the starting components and the corresponding physical-mixture/reference pattern. Preliminary indexing of 19 principal reflections yielded a tetragonal candidate lattice with  $a = b = 7.7411(5) \text{ \AA}$ ,  $c = 24.7182(10) \text{ \AA}$ , and  $V = 1481.2(5) \text{ \AA}^3$ , with an indexing figure of merit of approximately  $M_{20} = 23.0$ . The observed and calculated reflection positions showed generally consistent correspondence, supporting the proposed tetragonal lattice as a preliminary crystallographic description.

The PXRD indexing should, however, be regarded as a preliminary crystallographic assessment rather than a complete crystal-structure determination. The available diffraction profile was reconstructed from the displayed experimental pattern rather than obtained from the original raw instrumental dataset; consequently, the present analysis does not provide a definitive space-group determination, atomic coordinates, site occupancies, or interatomic geometries. The symmetry assessment establishes a tetragonal metric and supports a primitive lattice under the present indexing, while the available reflection conditions do not permit a unique assignment among the possible primitive tetragonal space groups.  $P4/mmm$  (No. 123) is therefore reported only as a candidate space group used for profile-consistency assessment.

Overall, the phase-equilibrium, chemical, FT-IR, SEM–EDS, thermal, and PXRD results provide mutually complementary evidence for the isolation of a distinct organic–inorganic crystalline phase with the proposed composition  $\text{ClCH}_2\text{COOH} \cdot \text{Ca}(\text{ClO}_3)_2 \cdot (\text{C}_2\text{H}_4\text{OH})_3\text{N}$ . The present study establishes its phase-equilibrium field, compositional characteristics, morphology, thermal behavior, and preliminary crystallographic parameters, while avoiding overinterpretation of the available PXRD data as a complete structural solution.

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