Supporting Information for

Shedding water: Using mechanochemistry to drive liquid assisted synthesis of the energetic complex Glycine-Magnesium Tetrahydrate

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The table below (Table S1) shows moisture content as it relates to drying the physical mixture, a dry physical mixture, and the 1-hour Lab RAM materials. The drying experiment examined the same 1:1 mole ratio of the physical mixtures and crude product as the main manuscript. For the dried physical mixture, to prevent a difference in the molar ratio, the materials were weighed and dried in the appropriate 1: 1 ratio prior to running the experiment. It demonstrates that the dried materials have lost some degree of hydration that may be playing a key role in the mechanochemical synthesis process. Additionally, the MC product is shown to demonstrate that the final product has lost water as part of the synthesis process.

Table S1. Table of the measured moisture content of the physical mixture, dried physical mixture, and of the 1-hour MC products.

Material	**% mass loss**
Physical Mixture	12.03
Dried Physical Mixture	3.90
1-hour Lab RAM	6.89

PXRD comparing the Lab RAM synthesized materials (Figure S1) highlights the evolution of the synthesized product as a function of time. The peaks in the 9 and 10° region of the PXRD were identified to evolve as a function of mixing time. The 15-minute and 30-minute samples appear to have significant differences between the materials, which is a result of the change in intensity of the characteristic peak at 28°. The peak intensity in the 15-minute and 30-minute diffraction patterns does evolve. Several key peaks decrease, such as the peaks at 23° and 24° during the synthesis process. Additionally, the 30-minute sample has a unique peak that has not been identified at ~36°, which does not correspond to any of the products or reactants. As

discussed later in Figure S5, the difference is likely caused by an inhomogeneous mixture that does not reach the final desired product as the bulk product until later (around 45-54 minutes) into the mixing process. The 1-hour mixing time eventually shifts the characteristic peak from the 28° to the 10° peak.

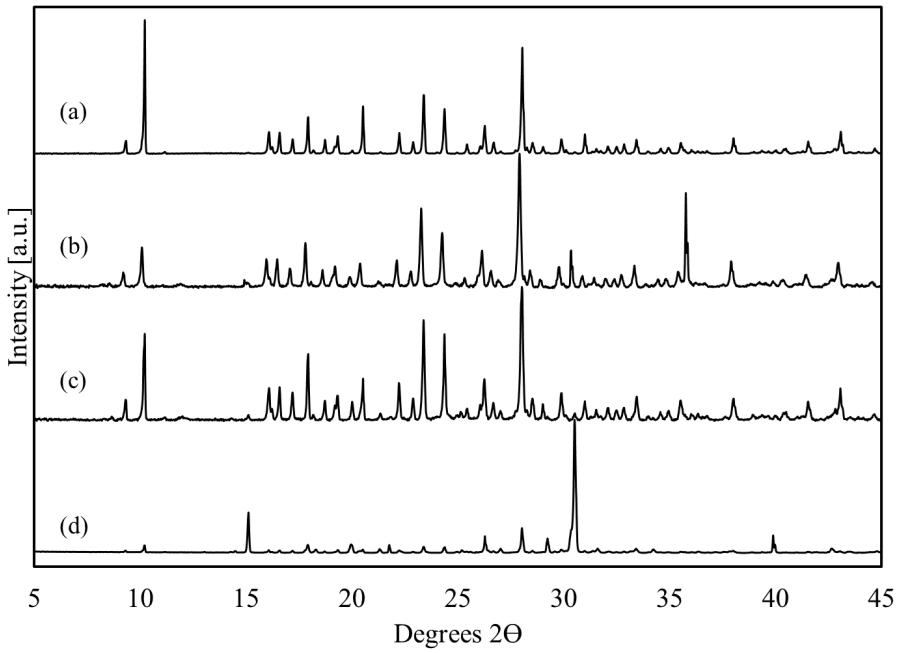

Figure S1. PXRD of (a) 1-hour lab RAM, (b) 30-minute lab RAM, (c) 15-minute lab RAM, (d) physical mixture.

From Figure 2, in the main manuscript, the peak at 30.5° was identified as a key peak of hydration for magnesium nitrate hexahydrate that is present for the diffraction pattern of the physical mixture. Figure S2 shows the diffraction pattern of the as-received magnesium nitrate hexahydrate and the dehydrated magnesium nitrate. Several peaks evolve as the material is dehydrated, but a key evolution is the reduction of the 30.5° peak, showing a relationship between that peak intensity and the hydration of magnesium nitrate. As such, the 30.5° peak was used to estimate the completeness of the reaction as a function of mixing time.

Figure S3 compares the initial physical mixture's relative intensity at the 30.5° peak to the three time points examined during the lab RAM process. It clearly shows a decrease in intensity of the peak as mixing time increases, showing a direct relationship between mixing time and the indicator of crystalline hydration.

Figure S4 compares the intensity of the 30.5° peak of the solvent evaporation material to the Lab RAM material (MC material). There is a significant difference in intensity, with the solvent evaporation material being significantly higher than that of the Lab RAM materials. This is likely caused by the incomplete conversion to the final products, as indicated by the Rietveld

refinement detailed in Table 1 of the main manuscript. In Table S2, the evolution of the 30.5° peak compared to the Rietveld refinement is shown. The comparison shows some agreement between the final product composition as determined from the refinement to the evolution of the 30.5° peak, with only the solvent evaporation product being an outlier. This could be the result of a different phase or stoichiometry of the product.

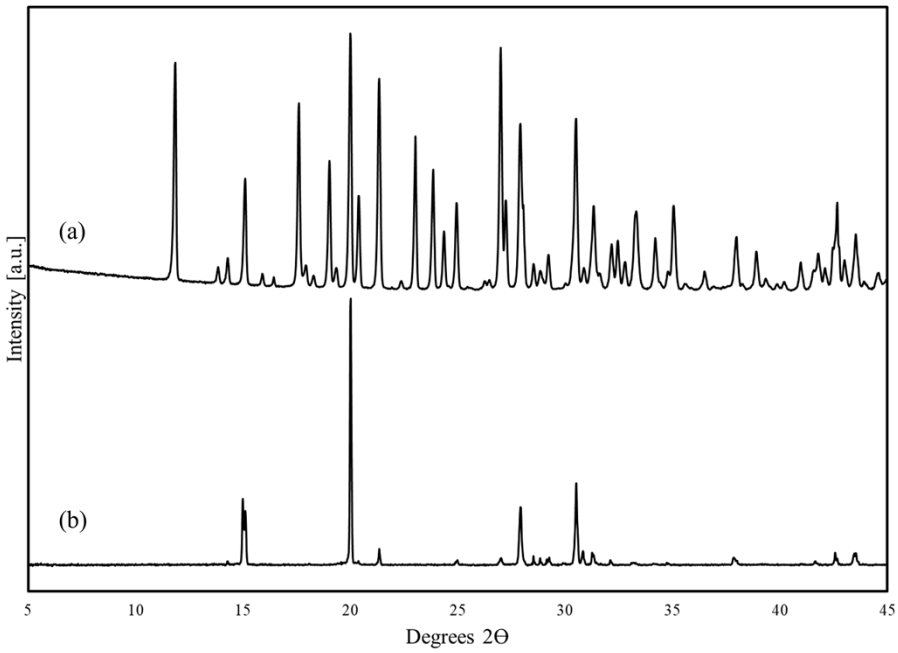

Figure S2. XRD comparison of (a) as-received magnesium nitrate and (b) dried magnesium nitrate.

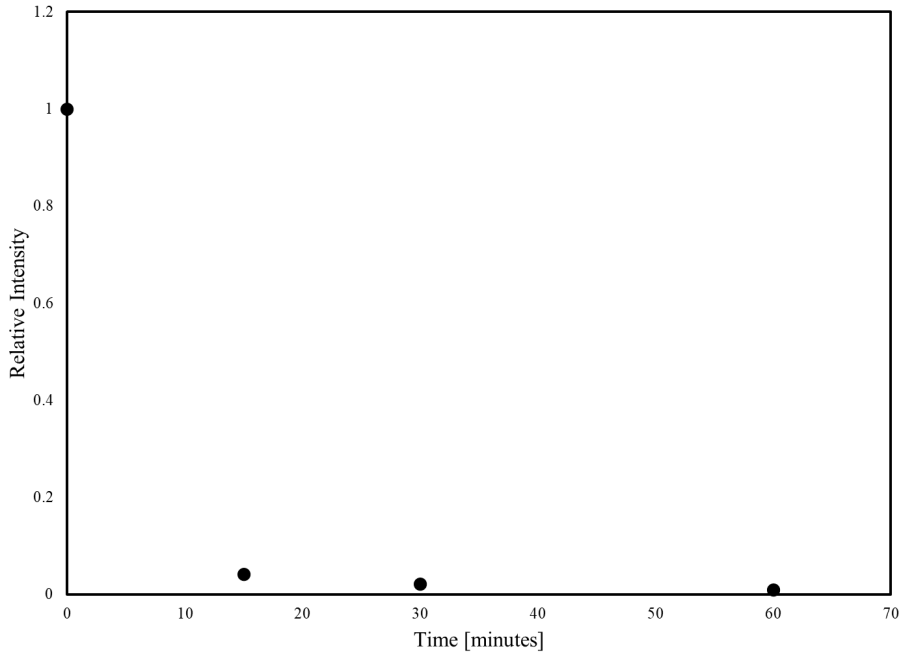

Figure S3. Plot of the relative intensity of the PXRD peak at 30.5° starting from a physical mixture at 0 minutes and going through the 1-hour lab RAM time.

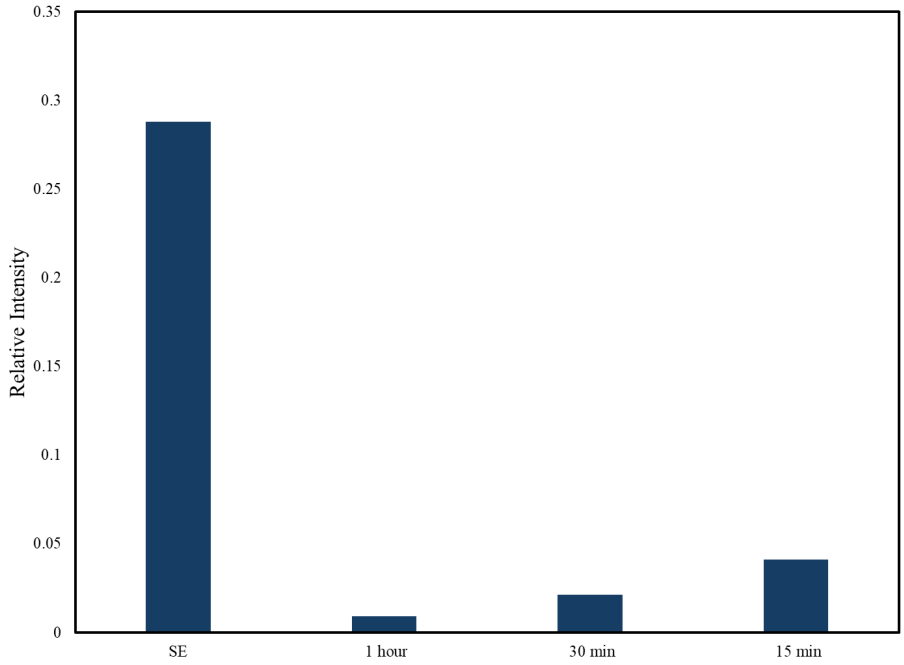

Figure S4. Plotting the relative intensity of the 30.5° peak, comparing the solvent evaporation products to the different lab RAM products.

Table S2. Comparison between the Rietveld refinement of the target product and to reduction of the 30.5° peak.

Sample	Rietveld mgn-gly wt%	30.5° Peak conversion
Solvent Evaporation	80.4 +/- 2.3	71%
1-hour Lab RAM	97.2 +/- 3.7	99%
30-min Lab RAM	95.7 +/- 4.9	98%
15-min Lab RAM	94.5 +/- 4.5	96%

When conducting the Lab RAM synthesis of the MC product, the power usage of the machine can be tracked and plotted as a function of time (Figure 5S). The power usage is constant leading up to the final synthesis of the wetted material seen as the final product in Figure 1. At the point the material agglomerates, there is a sudden oscillation in the power of the machine that then reduces to a net lower power requirement to achieve the same 30 G's acceleration. There are a variety of mixing times, where the same oscillation occurs between 45 minutes and 54 minutes.

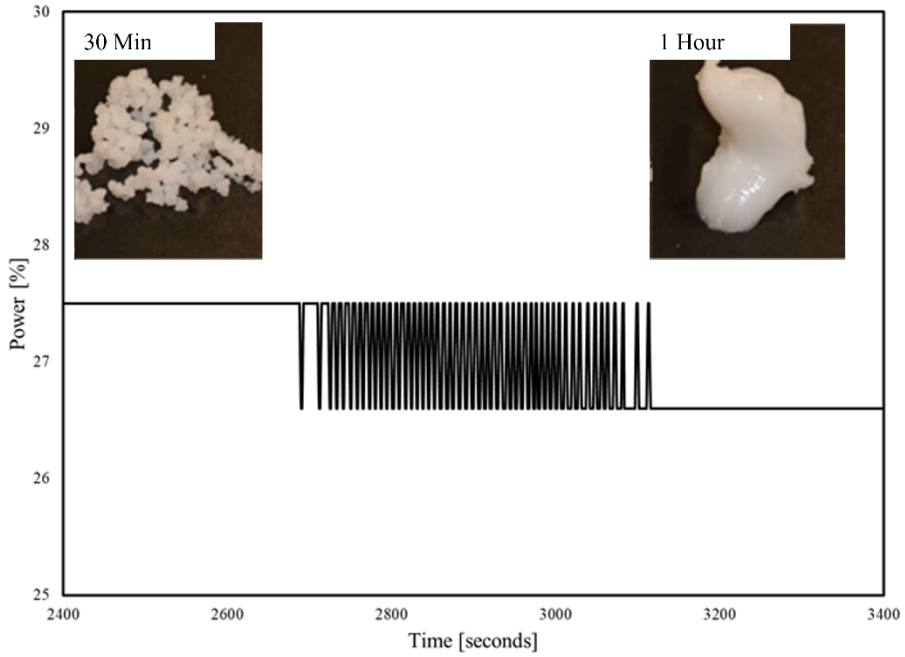

Figure S5. Snippet of the 1-hour Lab RAM power usage versus time, highlighting the region in which the material changes to an amorphous mass.

DSC-TGA Data

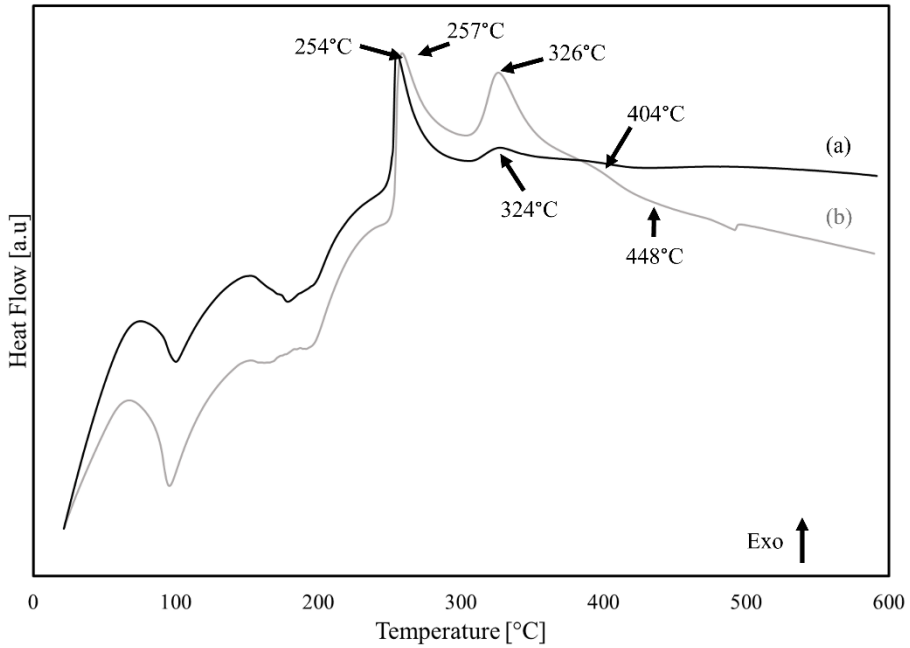

Figure S6. DSC of (a) 1 Hour LabRAM and (b) solvent evaporation products

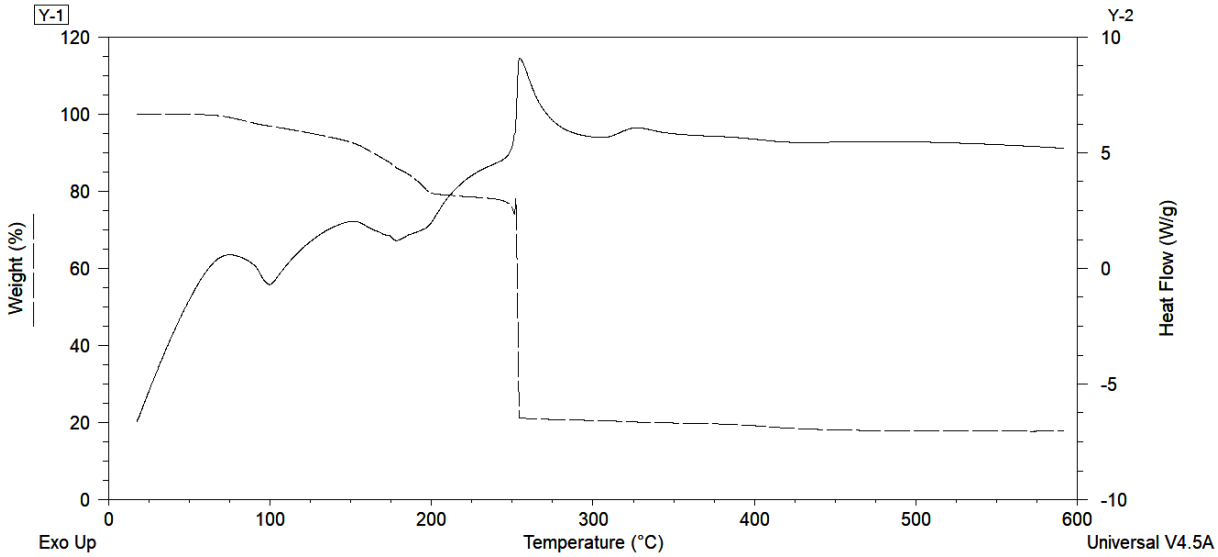

Figure S7. DSC-TGA 1 hour LabRAM

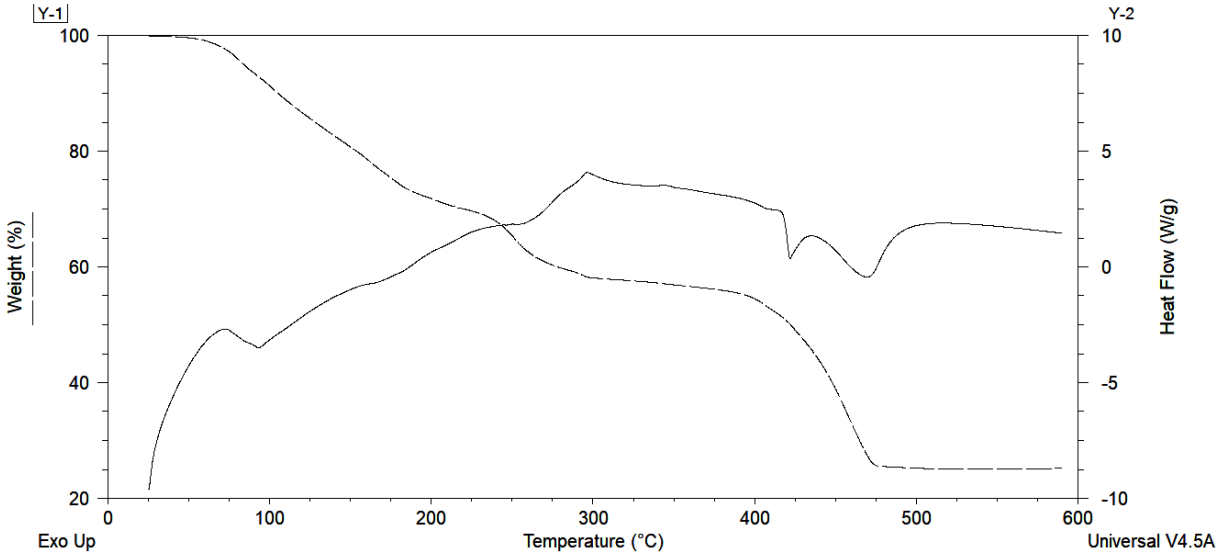

Figure S8. DSC-TGA 1 hour LabRAM of dried constituents

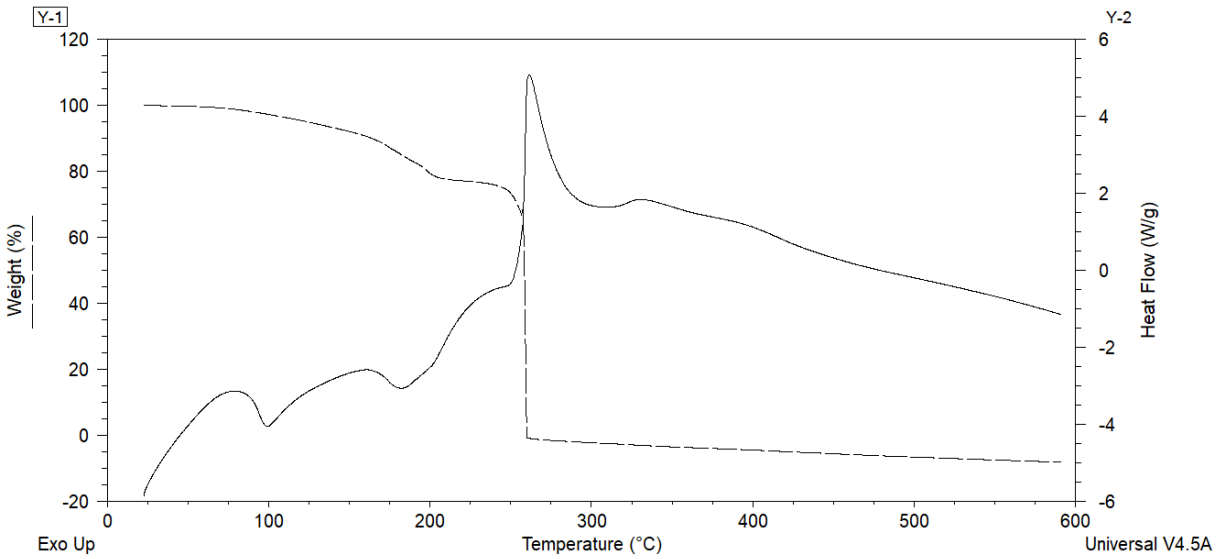

Figure S9. DSC-TGA 30-Minute LabRAM

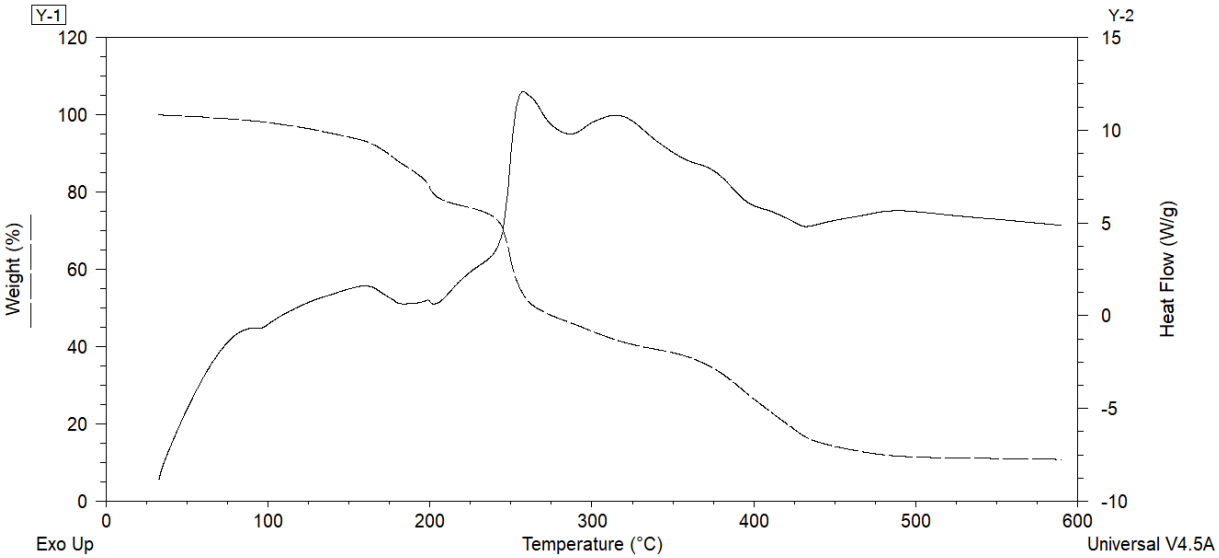

Figure S10. DSC-TGA 15 Minute LabRAM

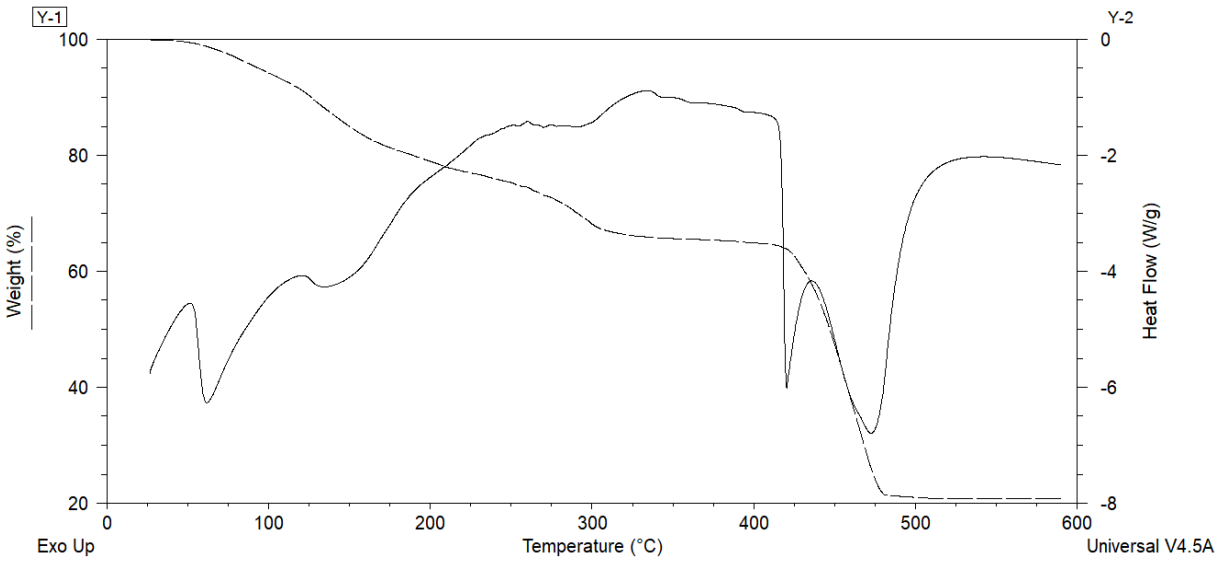

Figure S11. DSC-TGA Magnesium Nitrate Hexahydrate

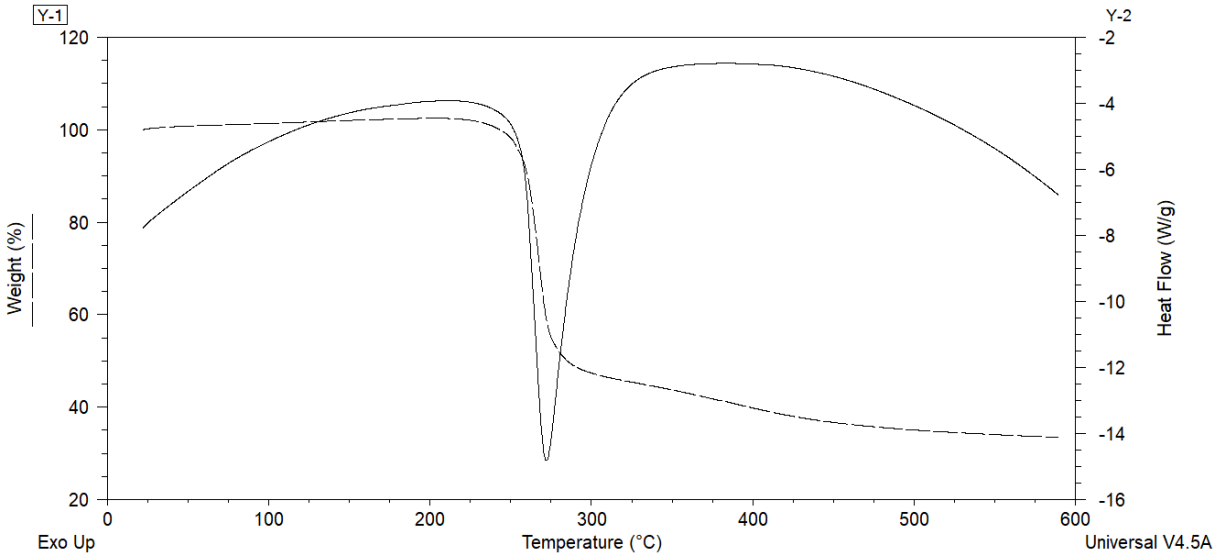

Figure S12. DSC-TGA Glycine

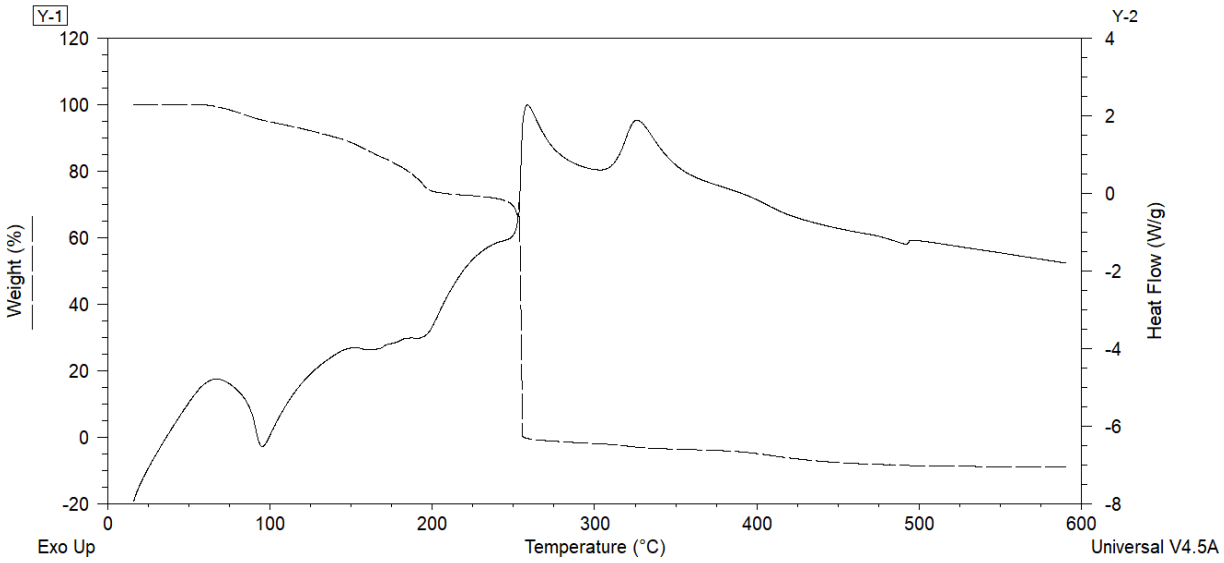

Figure S13. DSC-TGA solvent evaporation crystal

FTIR

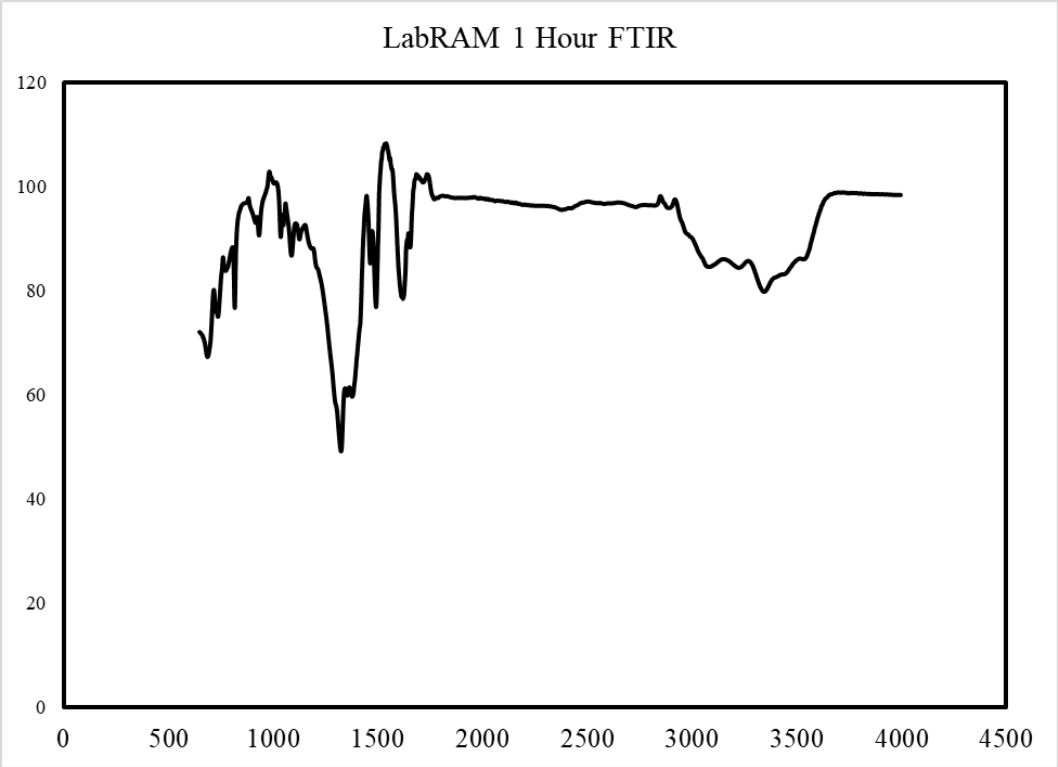

Figure S14. FTIR of 1-hour LabRAM

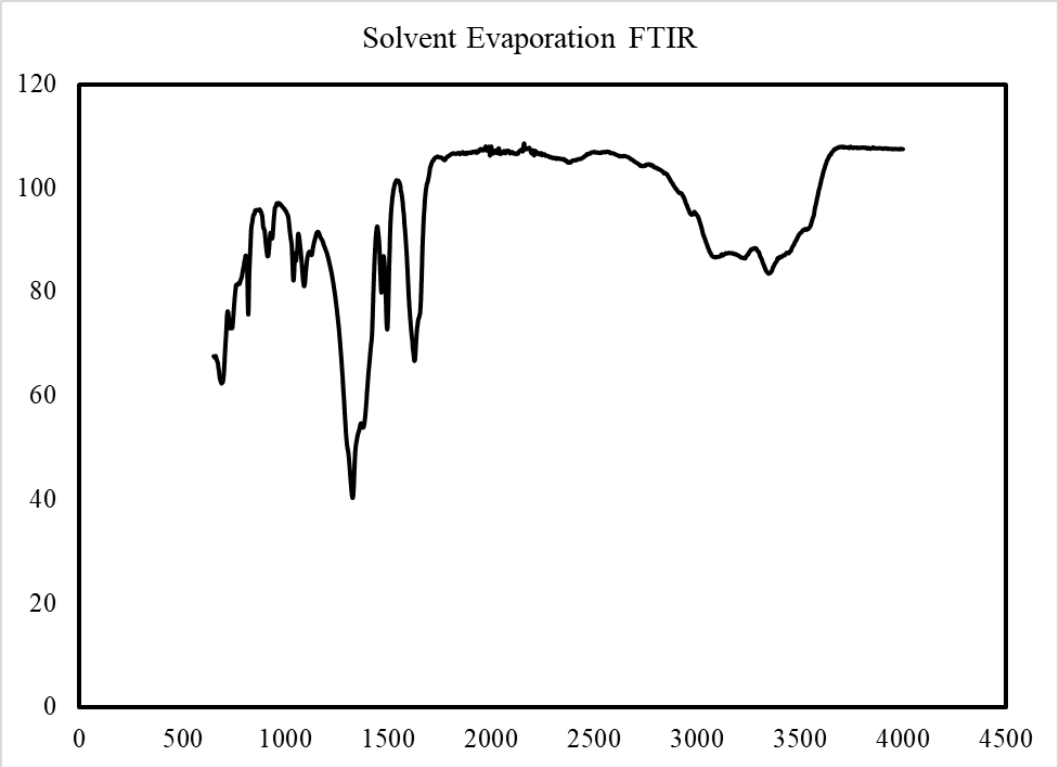

Figure S15. FTIR of solvent evaporation crystal

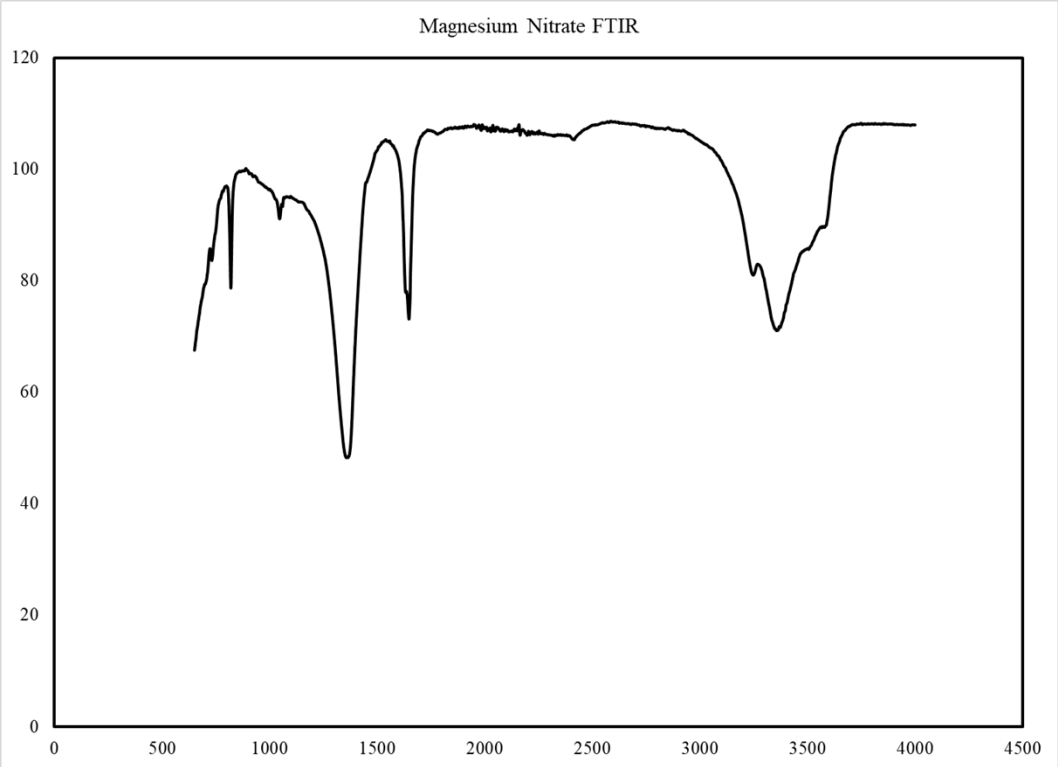

Figure S16. FTIR of Magnesium Nitrate Hexahydrate

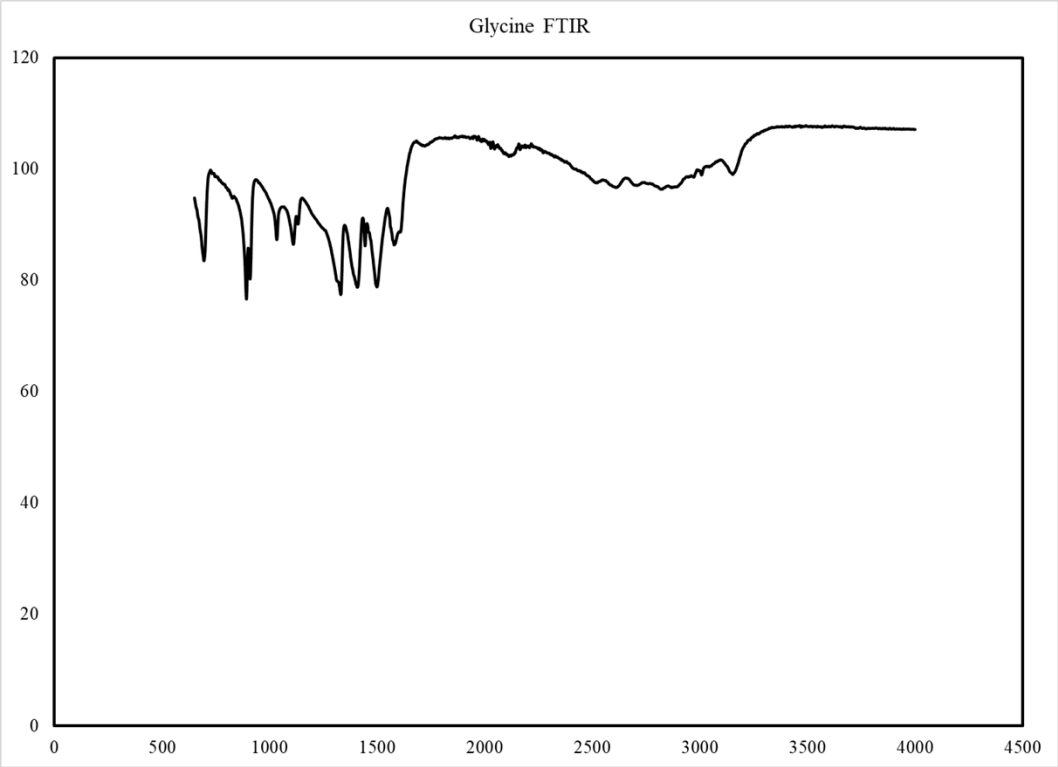

Figure S17. FTIR of glycine

XRD

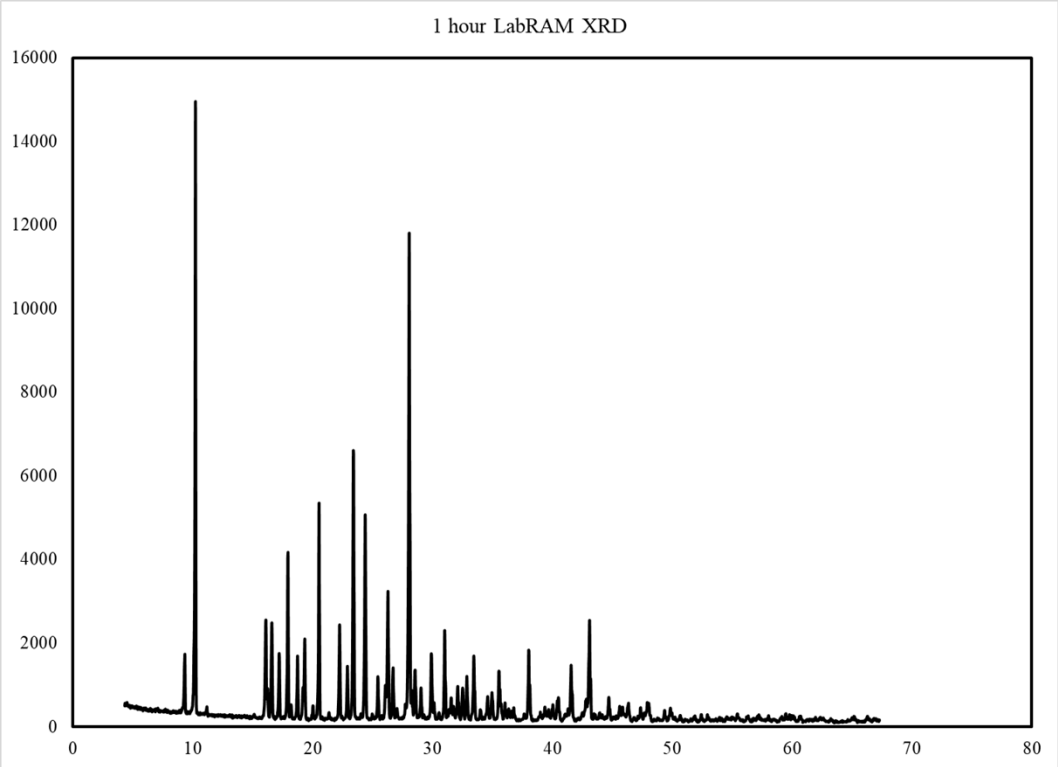

Figure S18. XRD of 1-hour LabRAM crystals

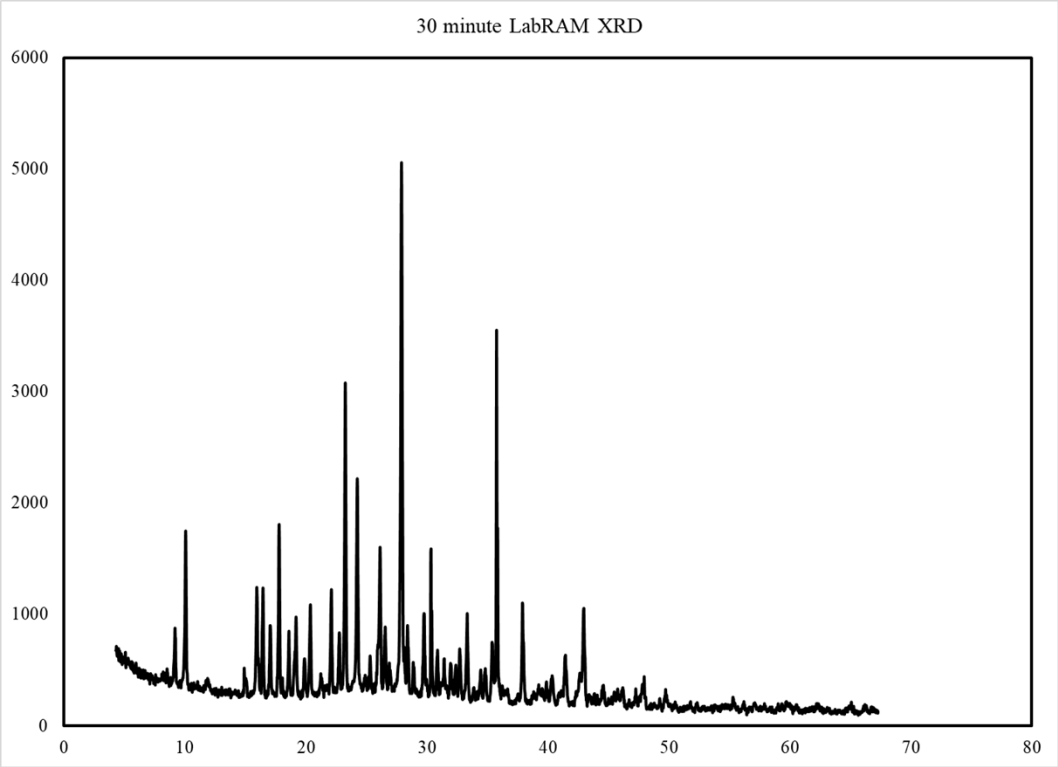

Figure S19. XRD of 30-minute LabRAM crystals

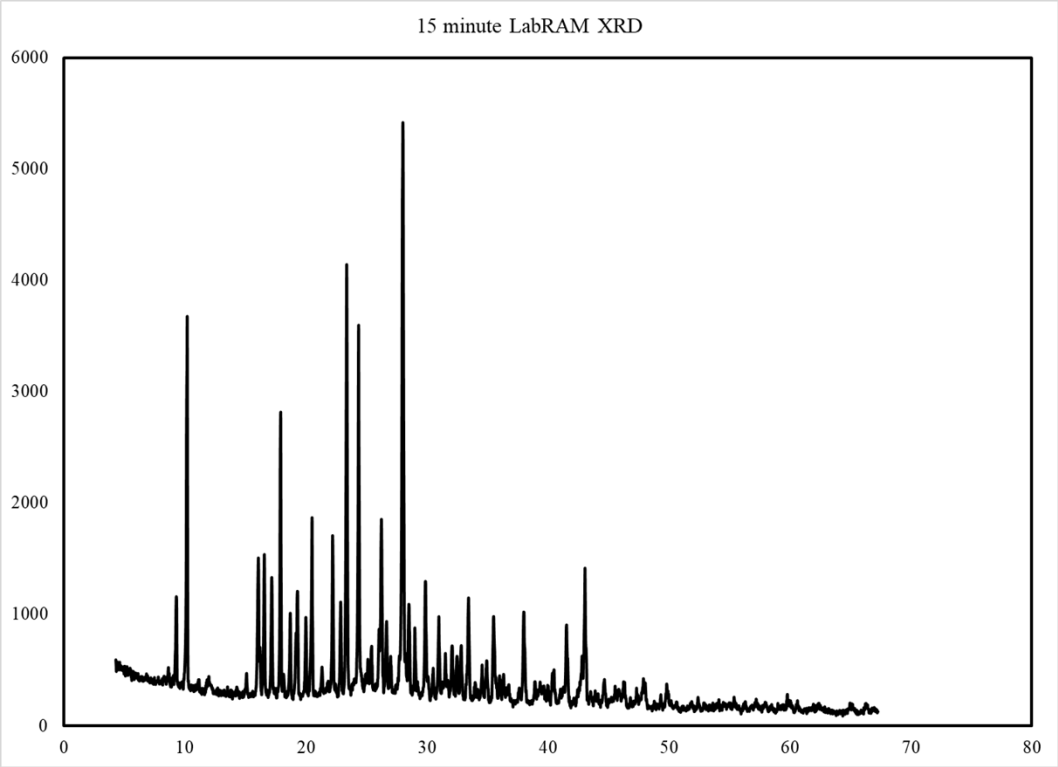

Figure S20. XRD of 15-minutes LabRAM crystals

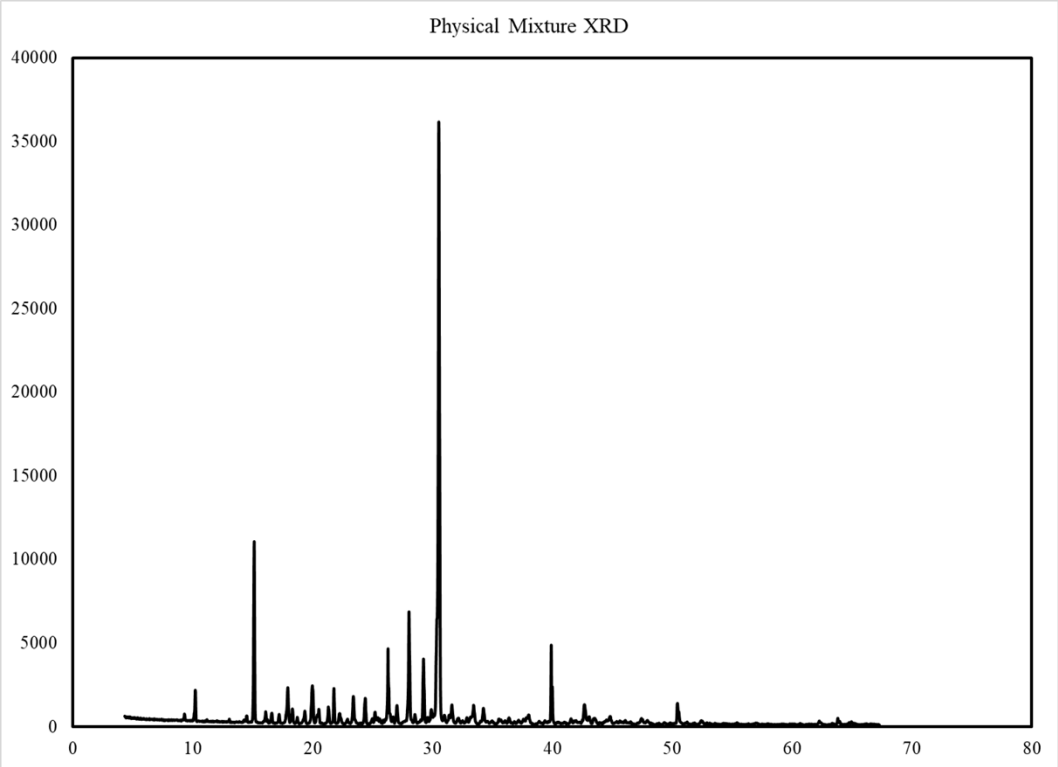

Figure S21. XRD of a physical mixture of the constituents

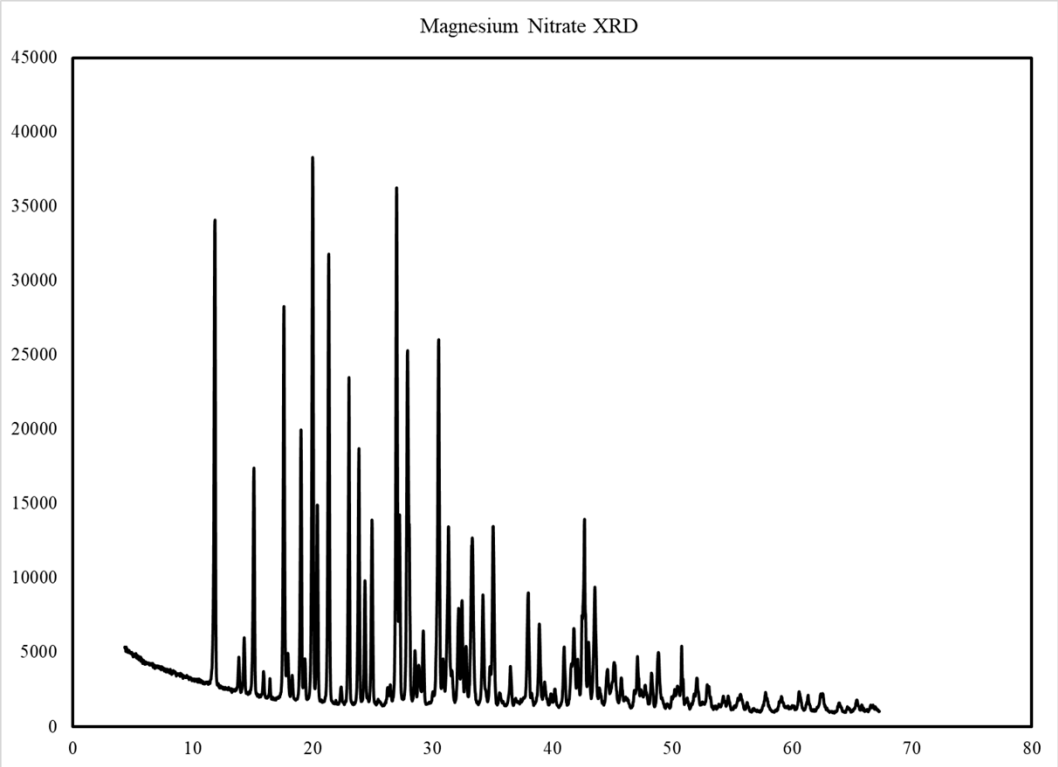

Figure S22. XRD of magnesium nitrate hexahydrate

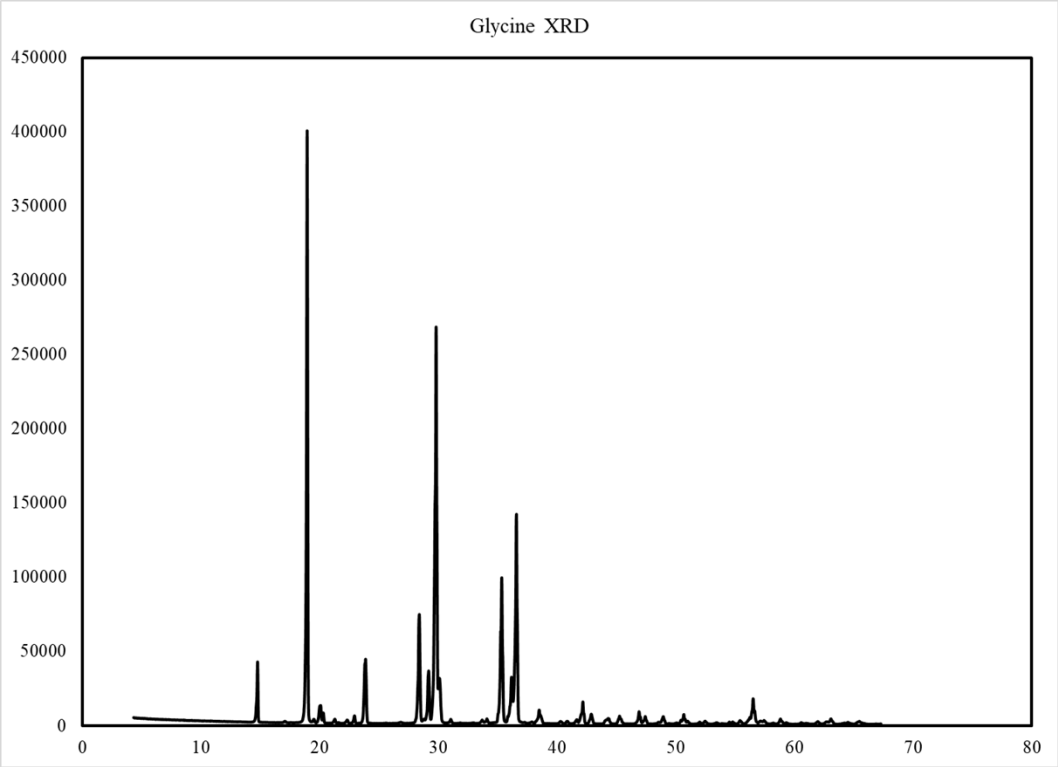

Figure S23. XRD of glycine

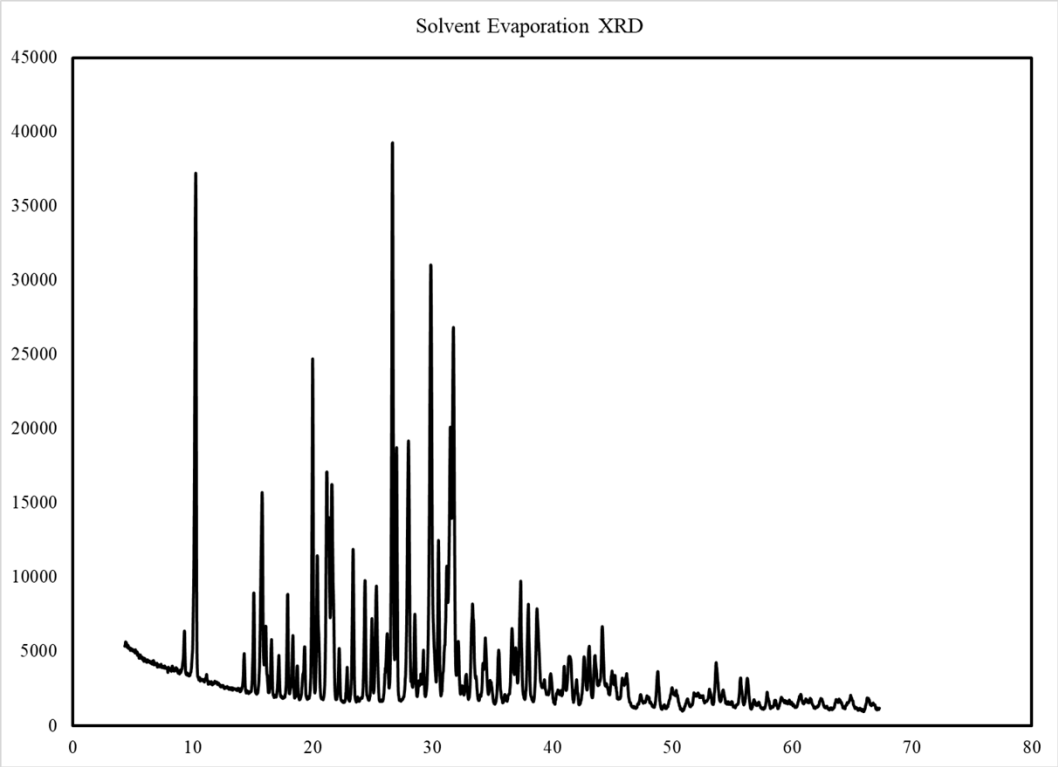

Figure S24. XRD of solvent evaporation crystals

The following figures, Figure S25-S30, are the refinement results from the pXRD for the different products. These are from the cobalt diffraction patterns prior to being shifted to the copper source, as reported in the main manuscript. The refinement error provides more discussion of the purity between the solvent evaporated products and the Lab RAM products. Specifically, when comparing the SE and MC products, the refinement was more successful for the targeted products, reaching a 20.54% R-factor for the MC products compared to the solvent evaporation product at 40.42%. These materials where refined with the specific phases of magnesium nitrate, glycine, and mgn-gly that were identified as the constituent components along with allowing the Jade software to automatically scan for additional materials that would have magnesium, nitrogen, carbon, hydrogen, or oxygen present. The Jade software did not find any additional phases that would improve the refinement. The error in the refinement shows that the products have unidentified materials present in the crude product. There are likely unreported/unidentified phases of the mgn-gly crystal and alternative stoichiometries that make further refinement impossible with the current crystallographic data available. The potentially unaccounted for alternative phases or stoichiometries results in reflections being missed in their entirety and reduces the quality of the overall refinement. However, it still indicates the Lab RAM method produces more of the known and targeted product.

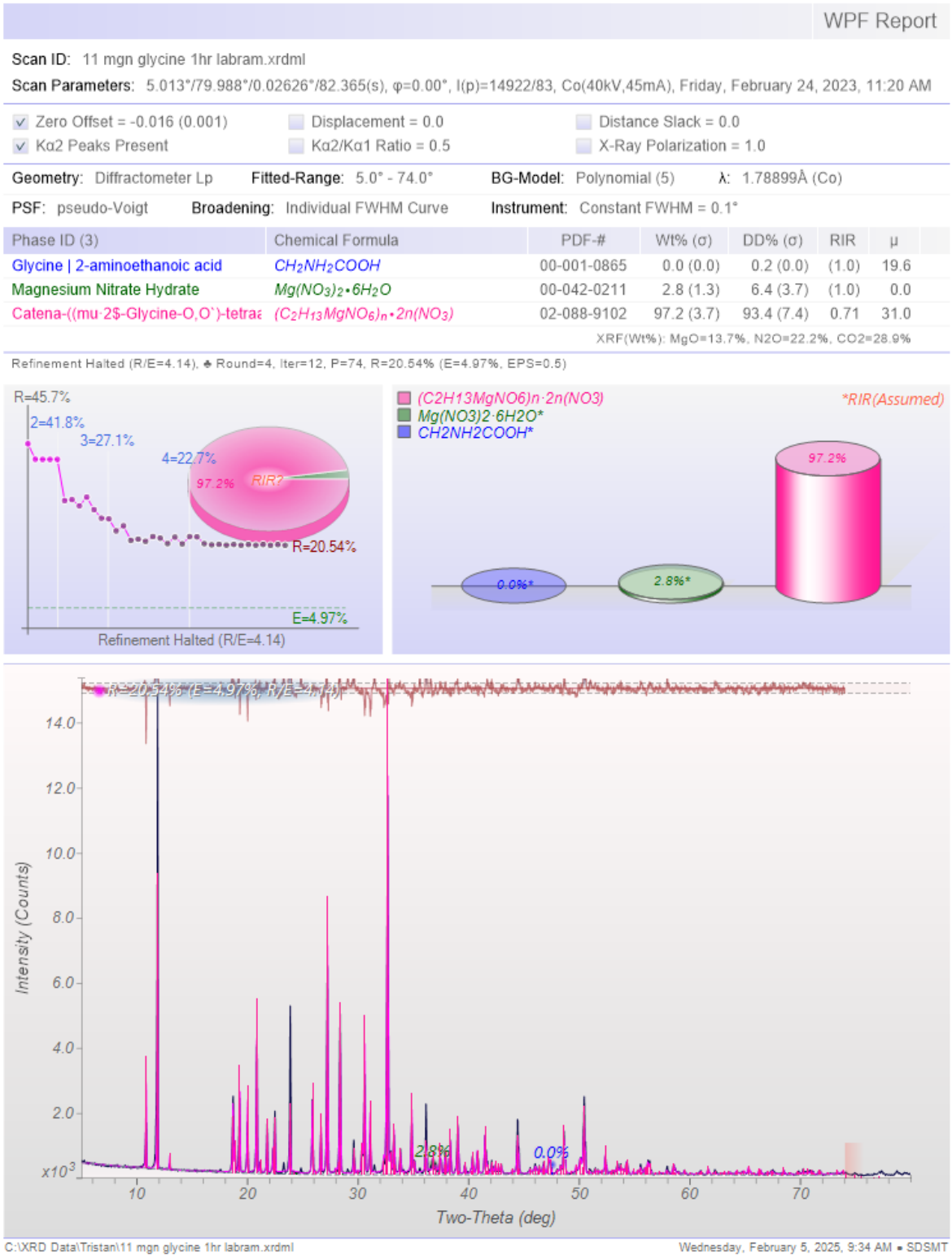

Figure S25. XRD refinement of the 1-hour LabRAM crystals

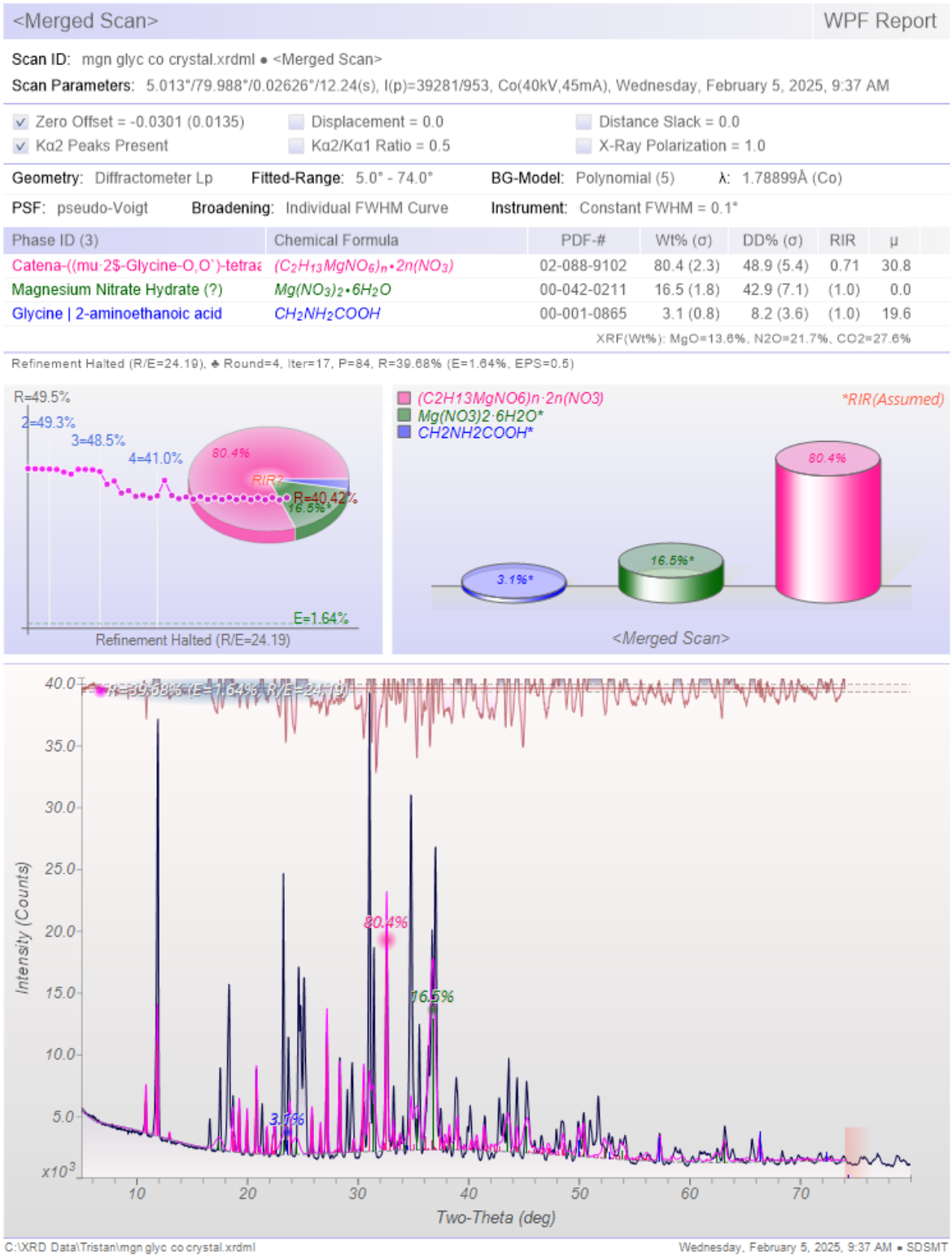

Figure S26. XRD refinement of the solvent evaporation crystals

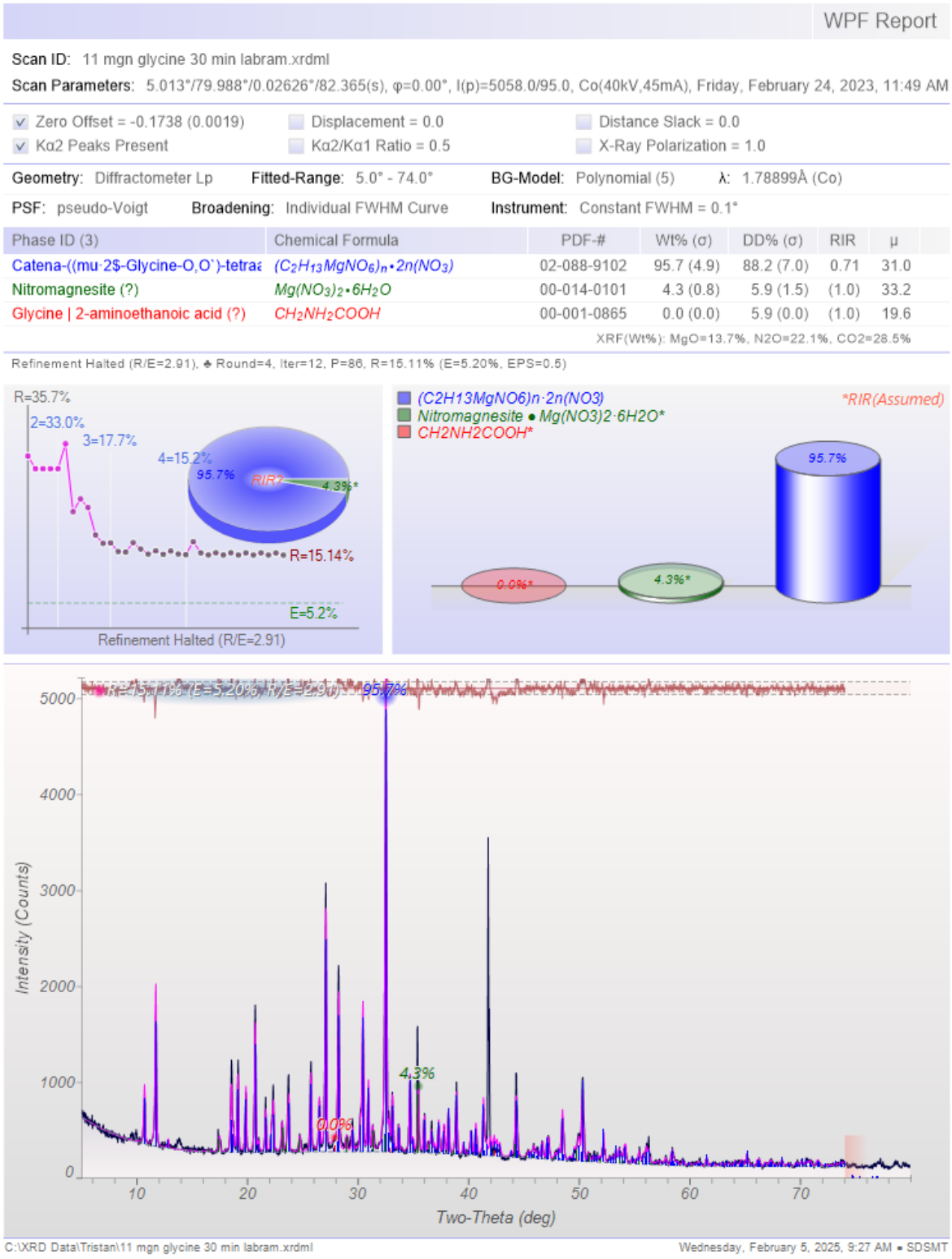

Figure S27. XRD refinement of the 30-minute LabRAM crystals

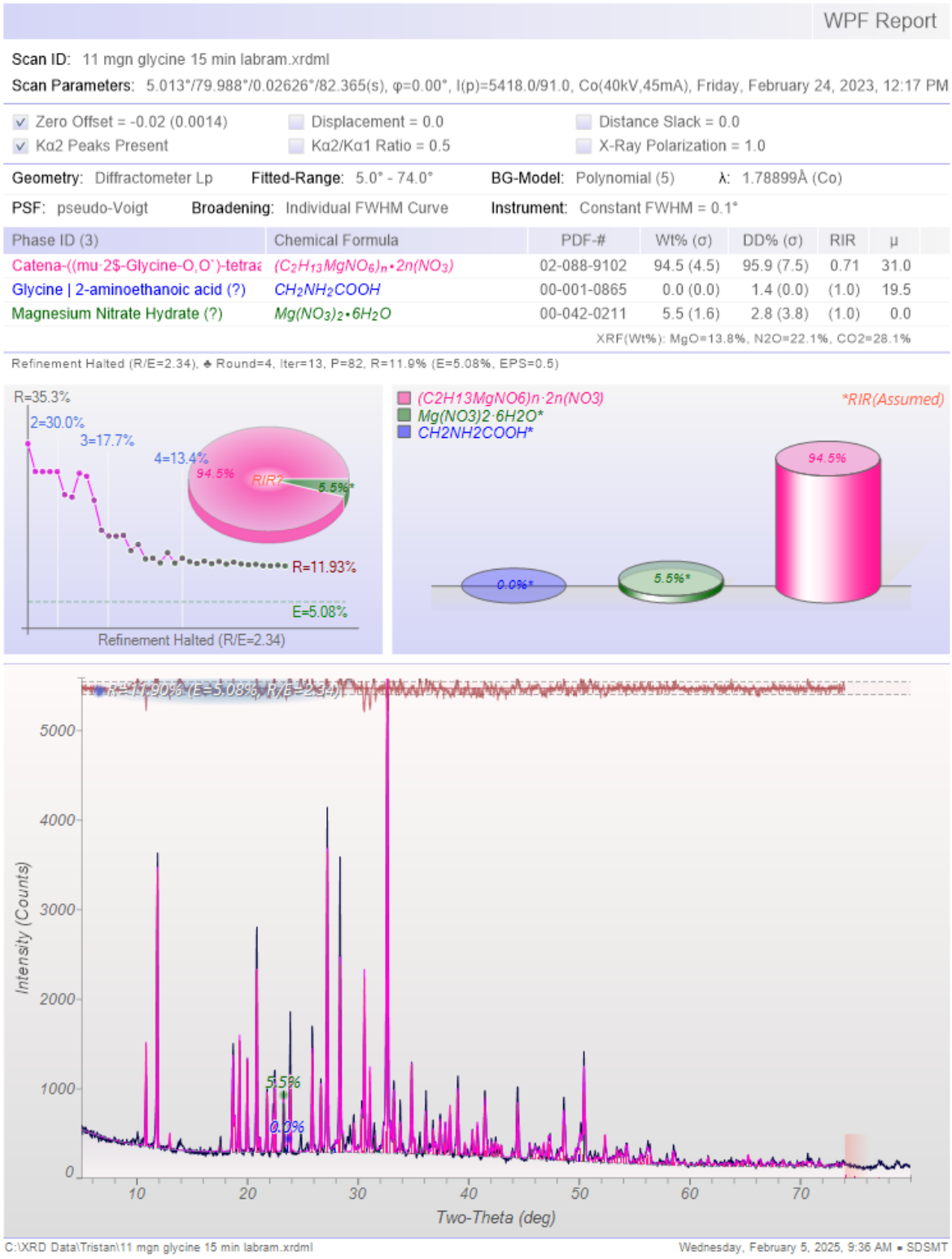

Figure S28. XRD refinement of the 15-minute LabRAM crystals

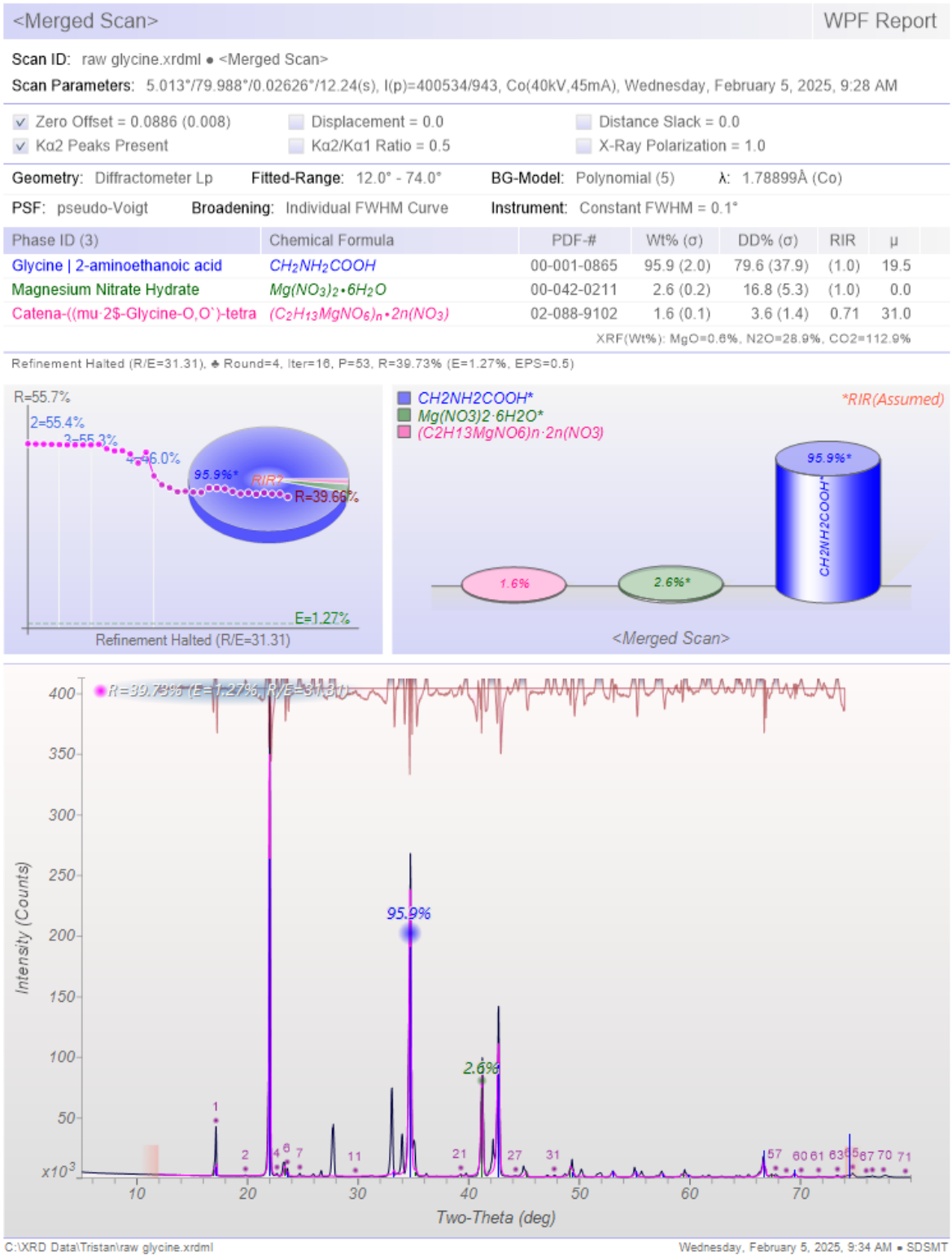

Figure S29. XRD refinement of the 1-hour LabRAM of dry reactants

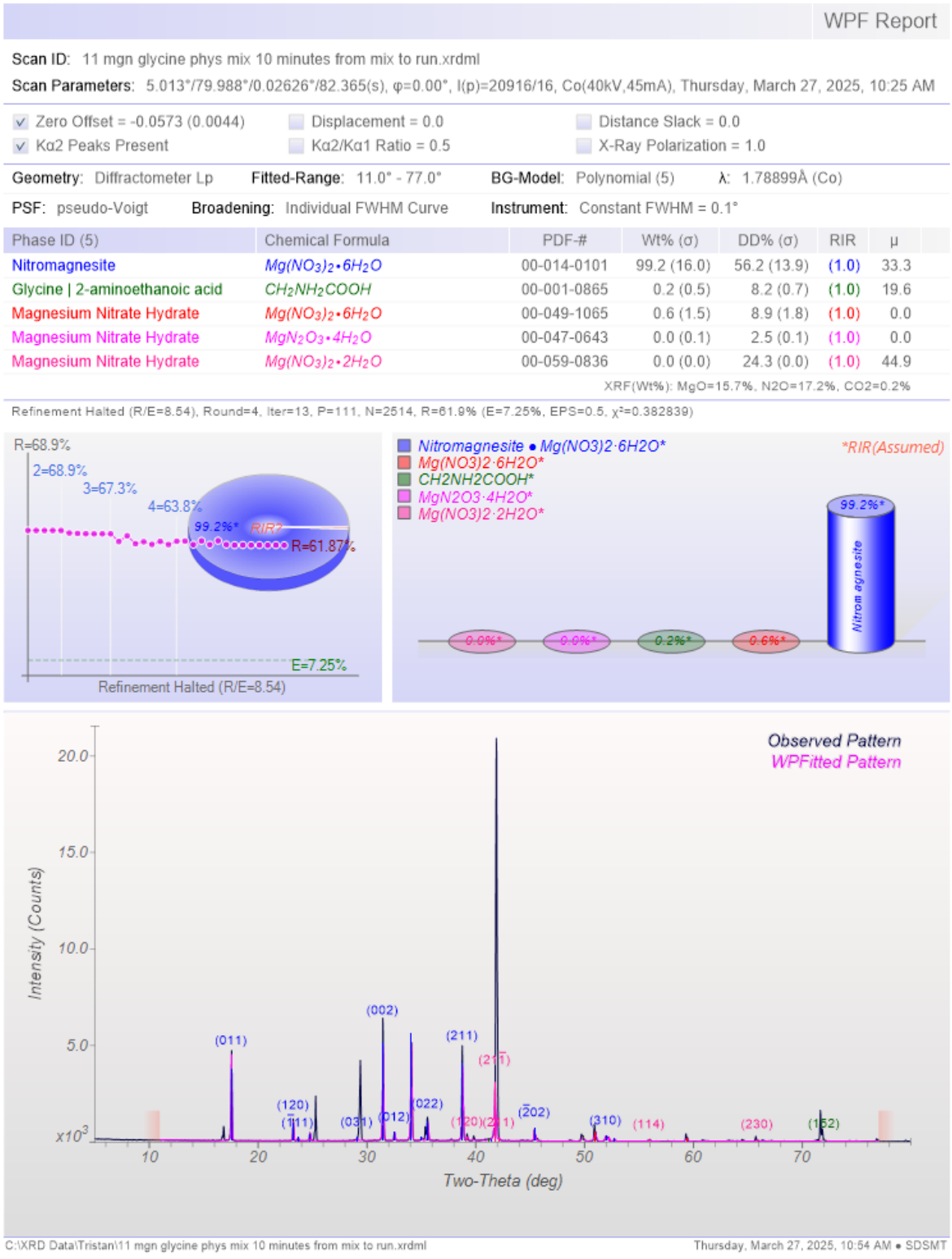

Figure S30. XRD refinement of the physical mixture