# Electronic Supplementary Information

## From molecular crystals to salt co-crystals of barbituric acid via the carbonate ion and an improvement of the solid state properties

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### SSNMR characterization of the salt co-crystals $NaBA \cdot HBA \cdot 2H_2O$, $KBA \cdot HBA \cdot 2H_2O$ and $KBA \cdot HBA_{0.5} \cdot 1.5H_2O$.

$NaBA \cdot HBA \cdot 2H_2O$ is characterized by one $BA^-$ and one neutral HBA in the asymmetric unit as confirmed by the $^{13}C$ signals at 78.8 and 39.7 ppm attributed to the CH and $CH_2$ respectively. The presence of two independent molecules in the unit cell is confirmed also by the $^{15}N$ peaks at 129.7, 121.9 and 117.2 ppm in a 2:1:1 ratio. These reflect the four different N-H···O HBs characterized by N-O distances of 2.765 and 2.802 Å for BA (signal at 129.7 ppm) and 2.874 and 2.849 Å for $BA^-$ (peaks at 121.9 and 117.2 ppm). The HB environments are in agreement with two proton resonances at 13.3 and 10.3 ppm for the strong (2.765 and 2.802 Å) and weaker (2.874 and 2.849 Å) HBs, respectively. Two water molecules are also present in the unit cell as confirmed by the integral values of the $^1H$ MAS spectrum and TGA data.

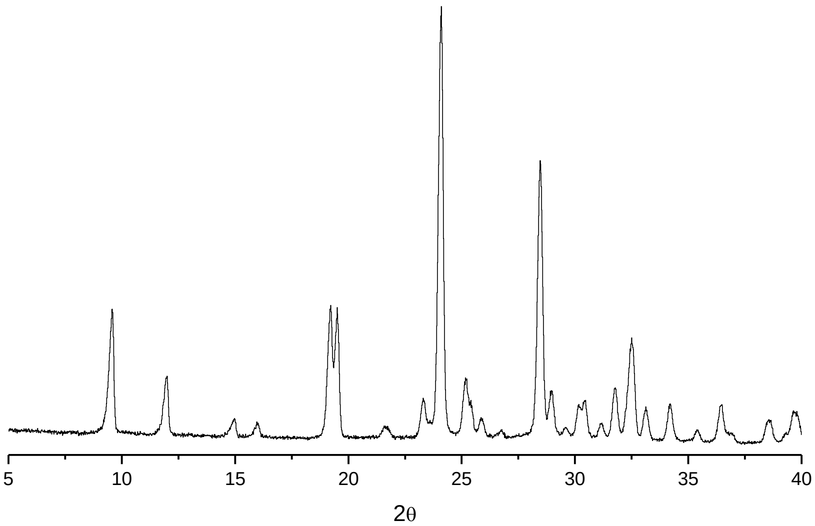
The $^{13}C$ CPMAS spectrum of $KBA \cdot HBA \cdot 2H_2O$ shows six sets of resonances in agreement with the presence of three independent $BA^-$ and three HBA molecules in the unit cell. This is particularly evident by the splitting of the CH resonances at 78.6, 78.1 and 77.5 ppm. The $^{15}N$ CPMAS spectrum is characterized by two groups of resonances centred around 130 (HBA NH) and 119 ppm ($BA^-$ NH). All HBs give rise to two signals in the $^1H$ MAS spectrum at 13.1 and 10.4 ppm associated to the strong (N-O distances < of about 2.81 Å) and weak interactions (N-O distances > of about 2.81 Å). The number of water molecules (6) as obtained from $^1H$ integrals agrees with that found in the X-Ray structure.

$^{13}C$ CPMAS spectrum of $KBA \cdot HBA_{0.5} \cdot 1.5H_2O$ shows the high symmetry of this structure. Indeed, the unit cell is characterized by one $BA^-$ (169.4, 154.6 and 79.6 ppm with a 2:1:1 ratio) and half molecule of HBA (173.0, 154.6 and 38.8 ppm with a 1:0.5:0.5 ratio). The C2 atoms of both HBA and $BA^-$ give rise to resonances overlapped at 154.6 ppm with total integral values of 1.5. This is confirmed also by the $^{15}N$ CPMAS spectrum where three peaks at 128.2, 118.5 and 118.1 ppm are present with the latter two being overlapped and belonging to the $BA^-$ ion.

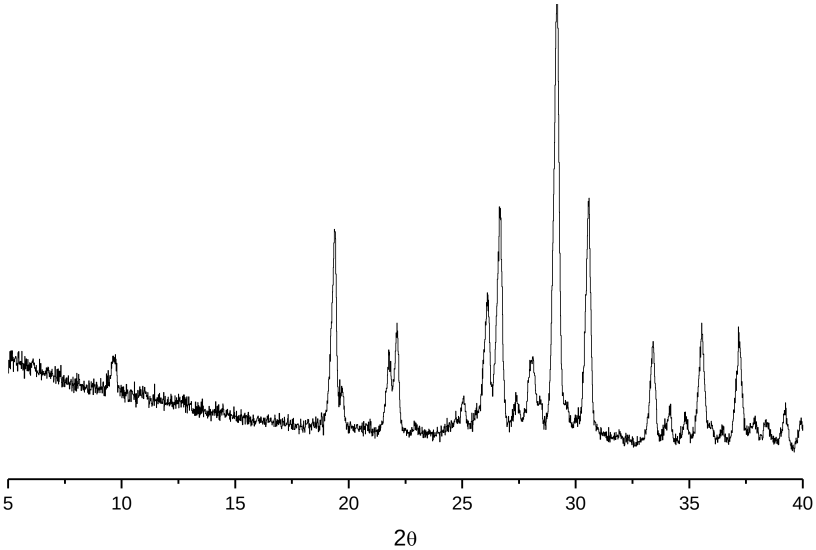
The number of water molecules was obtained by combining the $^1H$ MAS spectrum with TGA data.

The three HB environments (2.789 and 2.846 Å in $BA^-$ and 2.800 Å for BA) correspond to the three $^1H$ signals in the HB region at 13.7, 11.9 and 10.7 with a 2:1:2 ratio. The first and the last are associate to the $BA^-$ HBs (the strongest and the weakest) while the middle one to that of the HBA molecule.

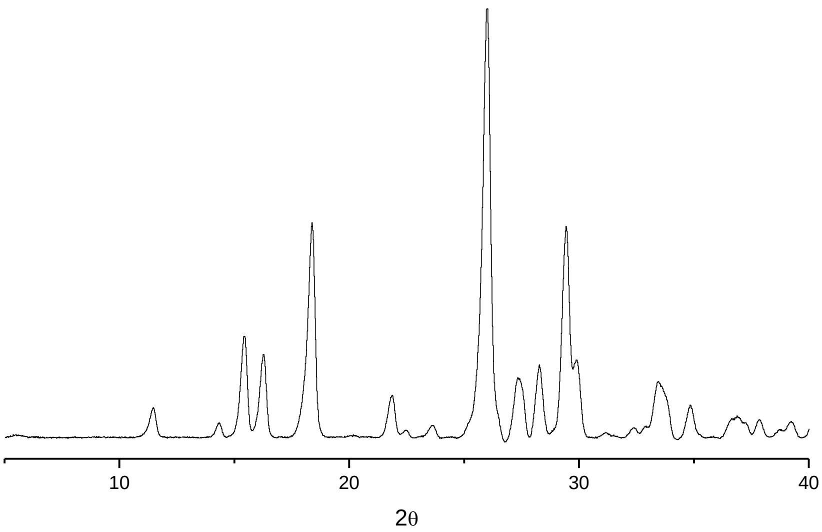
**Figures S1:** XRPD patterns of all prepared salts.



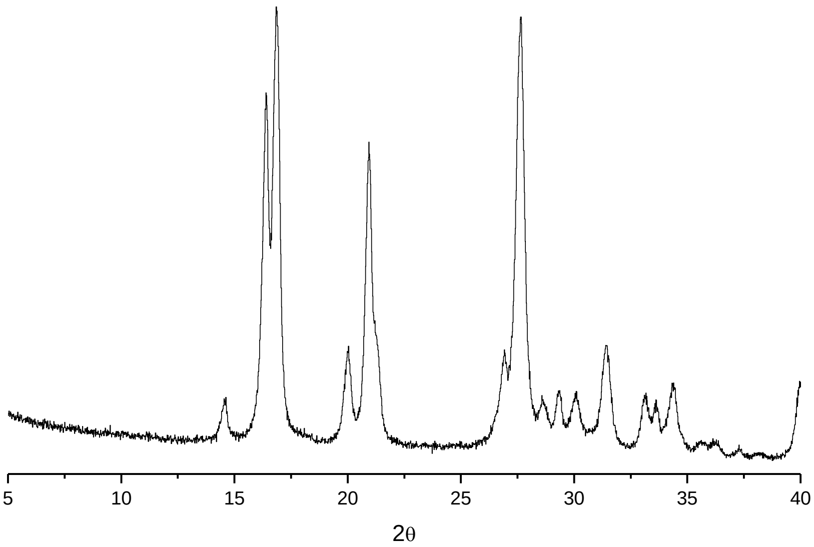
Experimental pattern of NaBA·1$H_2O$



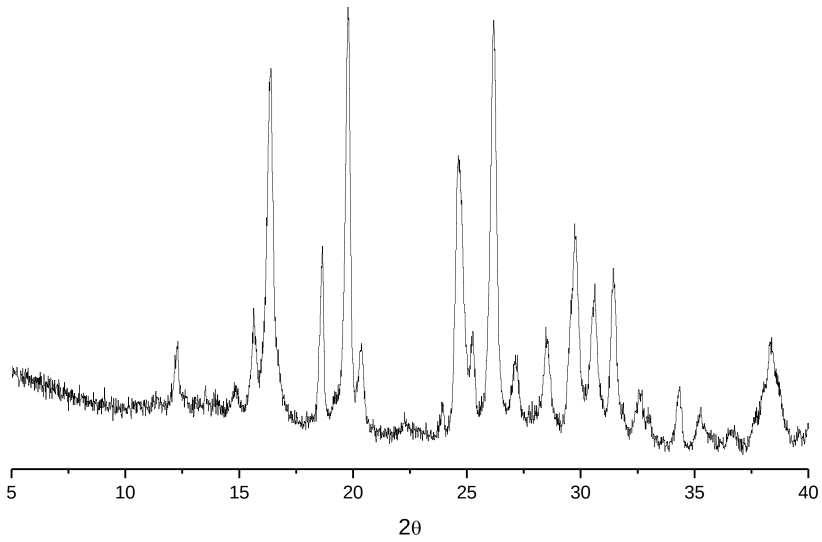
Experimental pattern of KBA



Experimental pattern of $MgBA_2 \cdot 2H_2O$

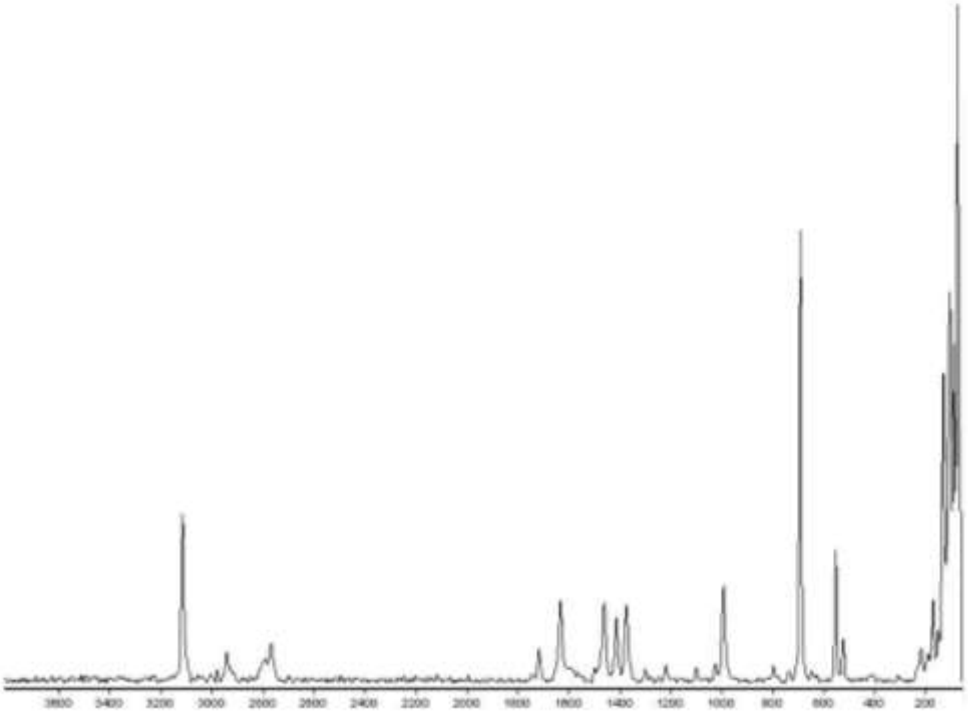


Experimental pattern of $MgBA_2$

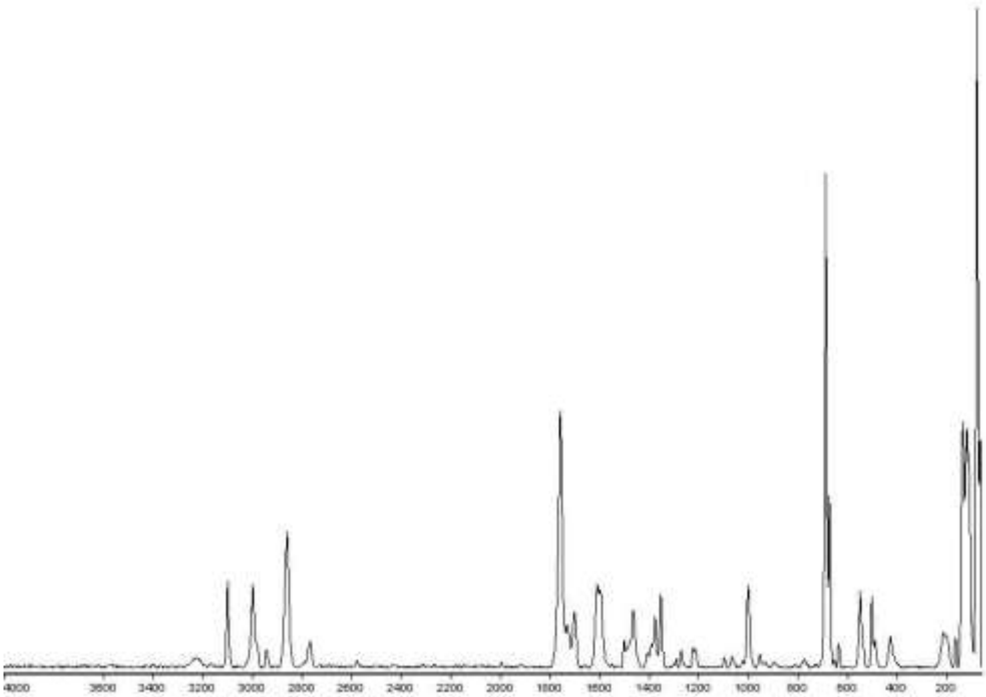


Experimental pattern of $CaBA_2\cdot 3H_2O$

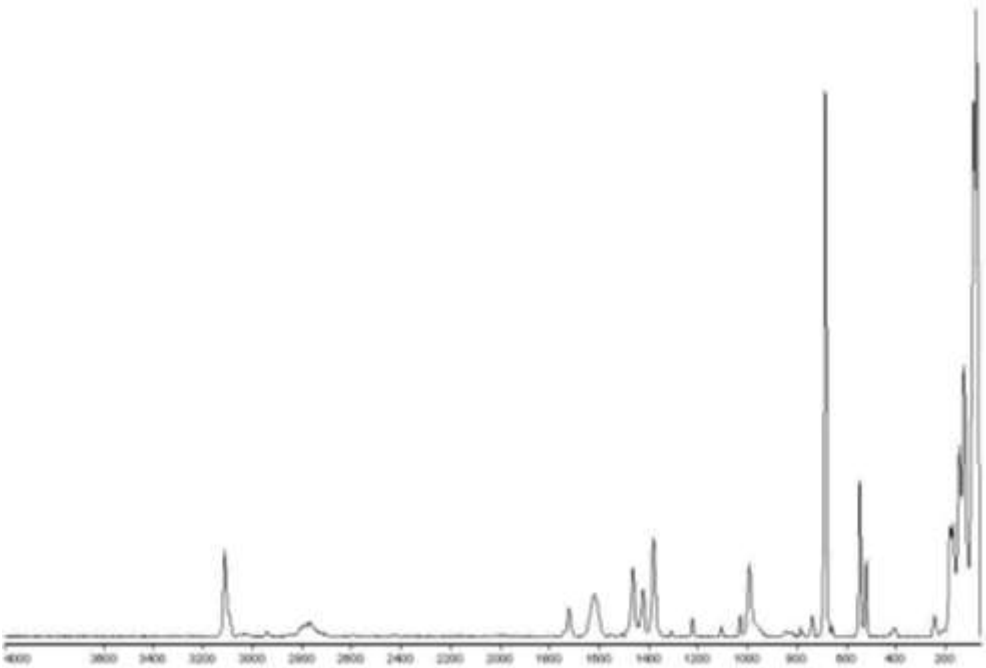
**Figures S2:** Raman spectra of all prepared compounds.



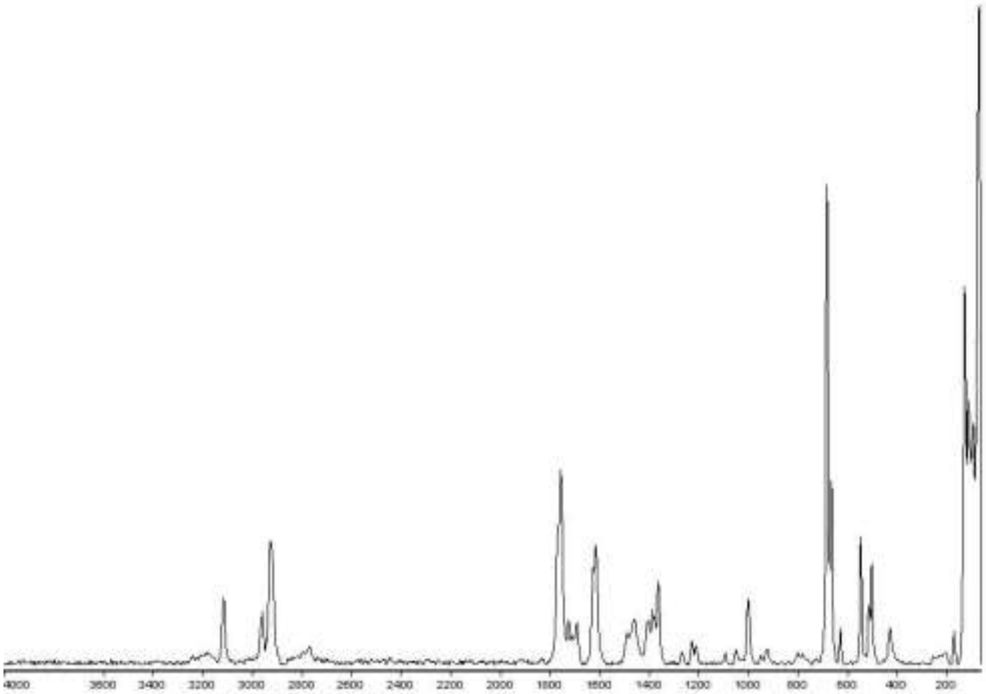
Raman spectrum of the salt $NaBA\cdot 1H_2O$.



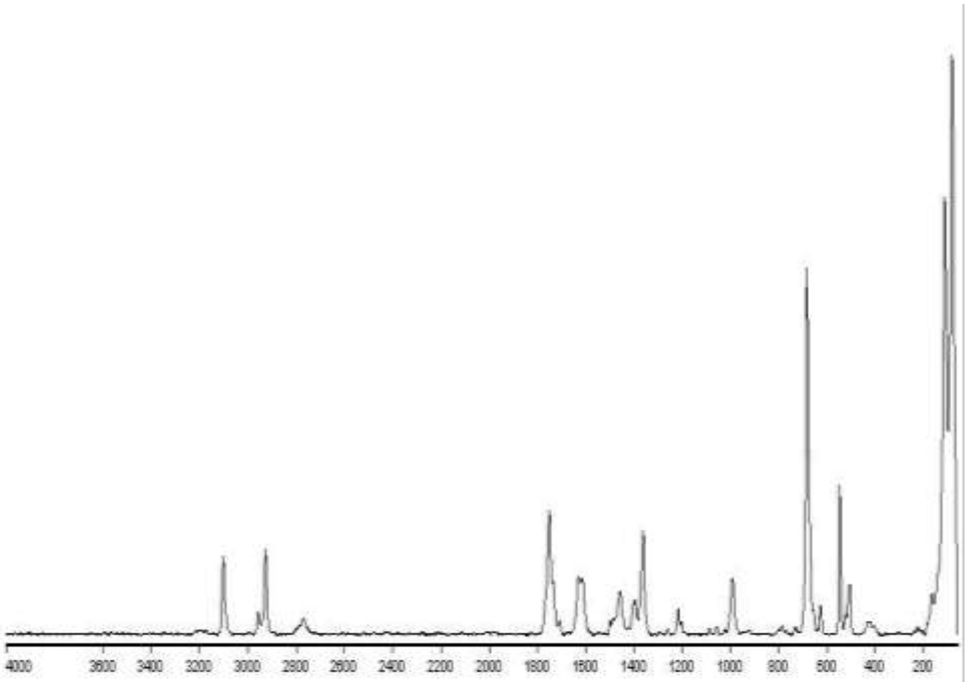
Raman spectrum of the salt co-crystal NaBA·HBA·$2H_2O$.



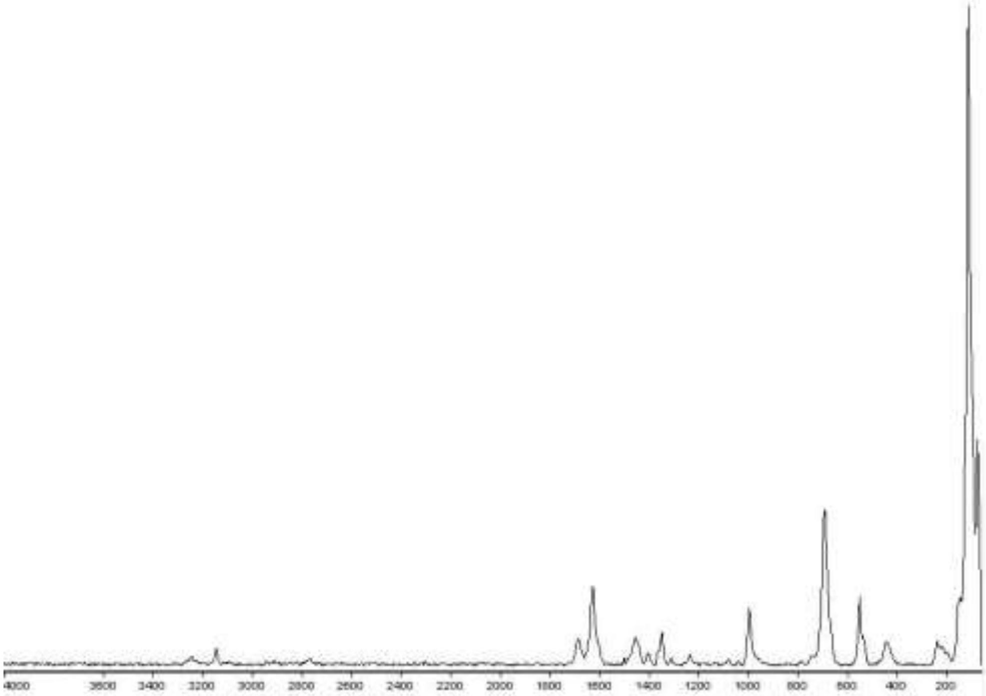
Raman spectrum of the salt KBA.



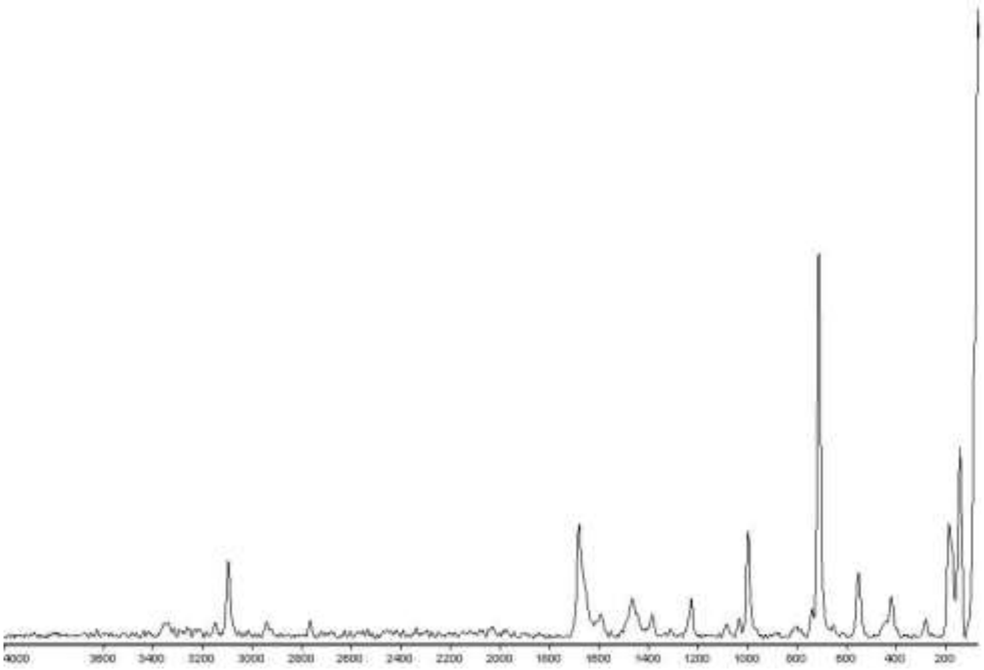
Raman spectrum of the salt co-crystal KBA·HBA·$2H_2O$.



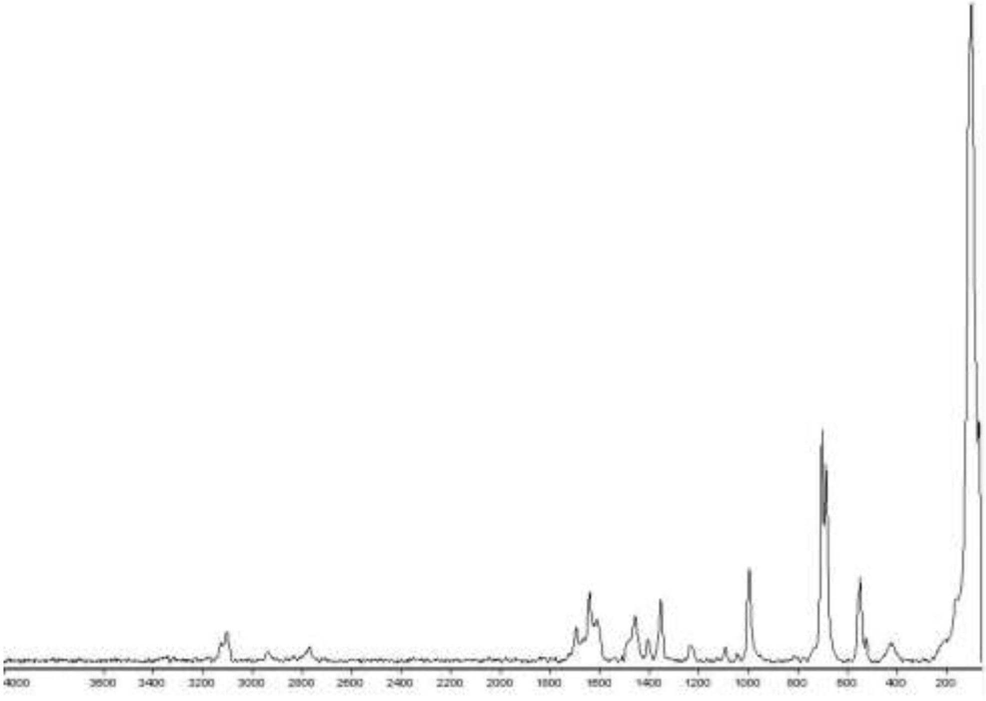
Raman spectrum of the salt co-crystal KBA·$HBA_{0.5}$·$1.5H_2O$.



Raman spectrum of the salt $MgBA_2 \cdot 2H_2O$.

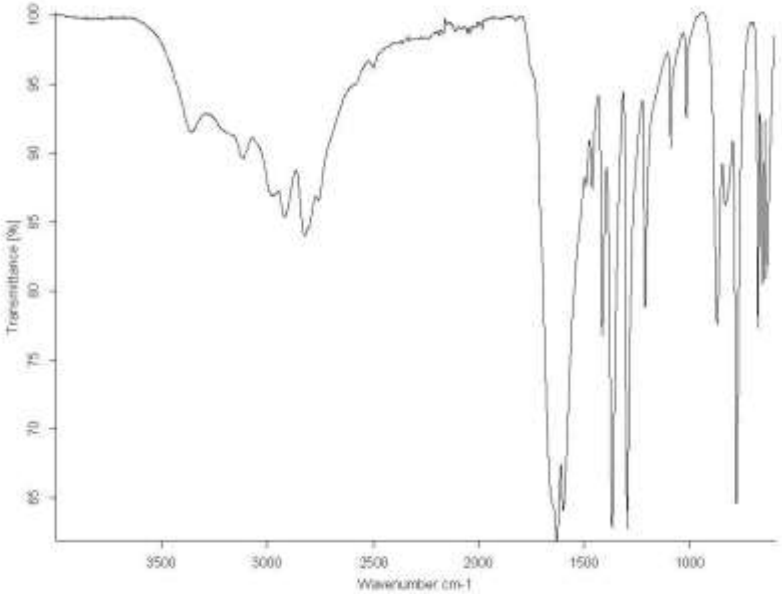


Raman spectrum of the salt $MgBA_2$.

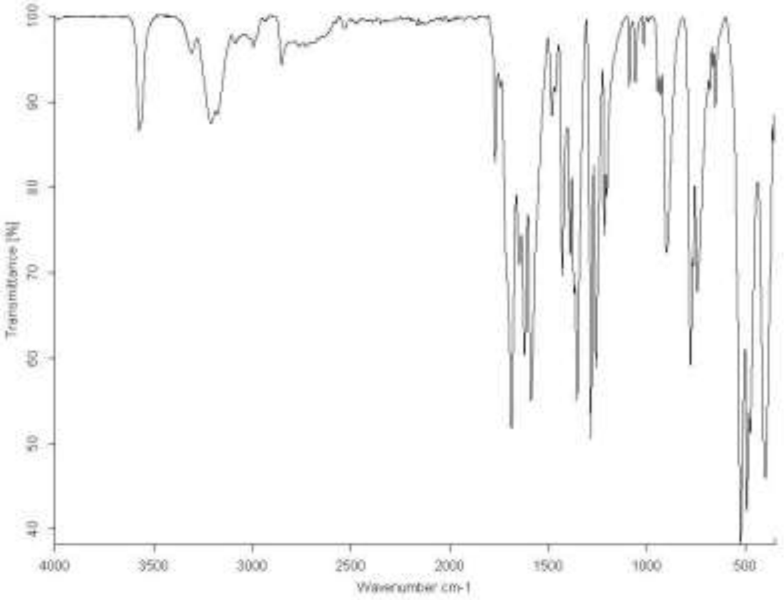


Raman spectrum of the salt $CaBA_2 \cdot 3H_2O$.

**Figures S3:** IR (ATR) spectra of all prepared compounds.



IR (ATR) spectrum of $NaBA \cdot 1H_2O$.



IR (ATR) spectrum of NaBA·HBA·2$H_2$O.

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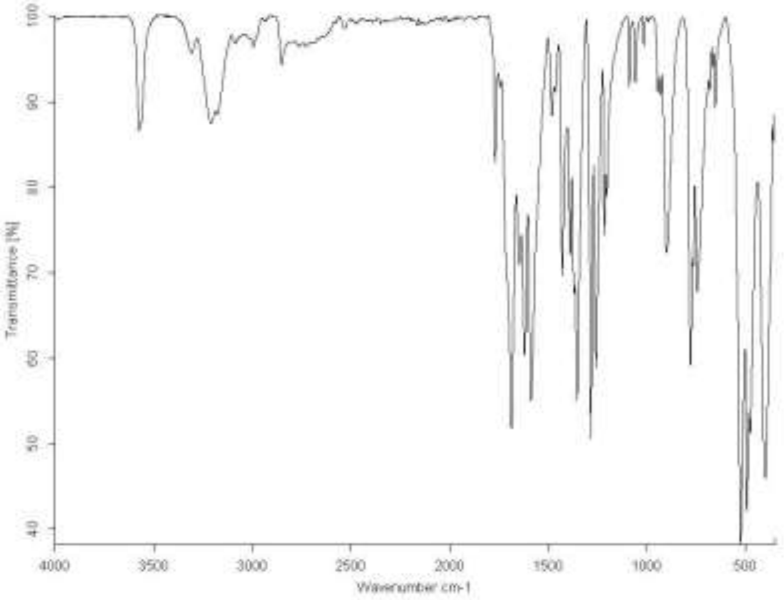
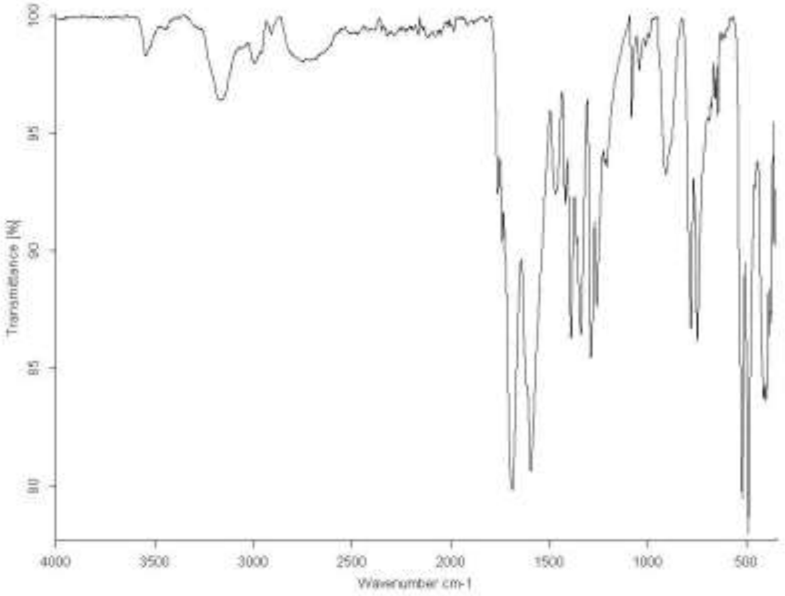
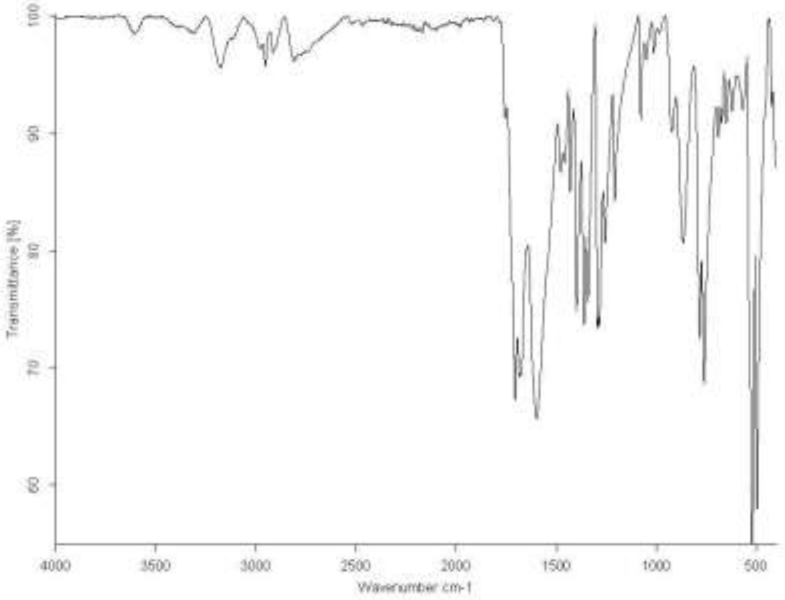


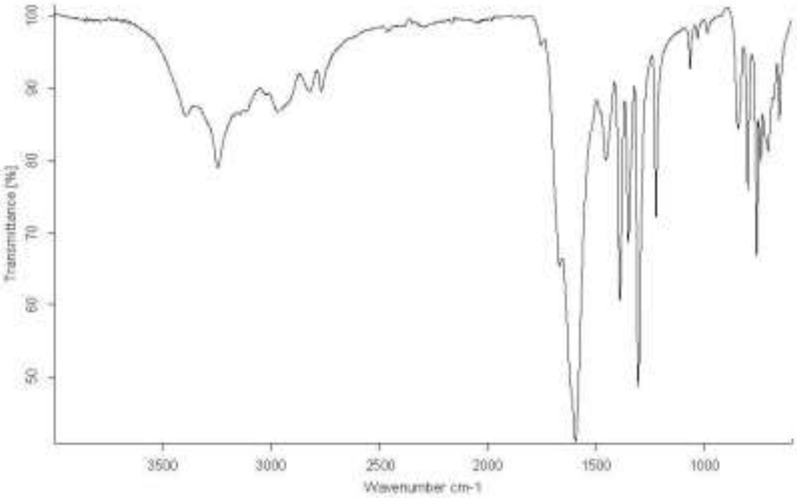
IR (ATR) spectrum of KBA.



IR (ATR) spectrum of KBA·HBA·$2H_2O$.



IR (ATR) spectrum of KBA·$HBA_{0.5}$·$1.5H_2O$.



IR (ATR) spectrum of MgBA$_2$·2H$_2$O

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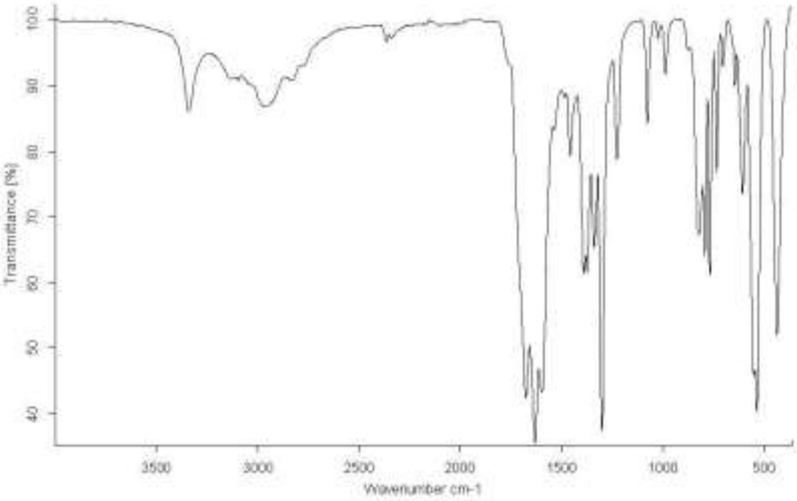
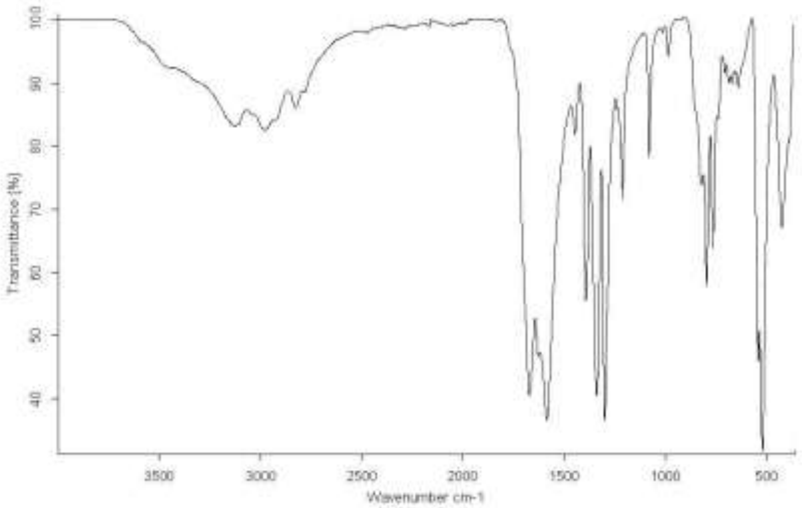
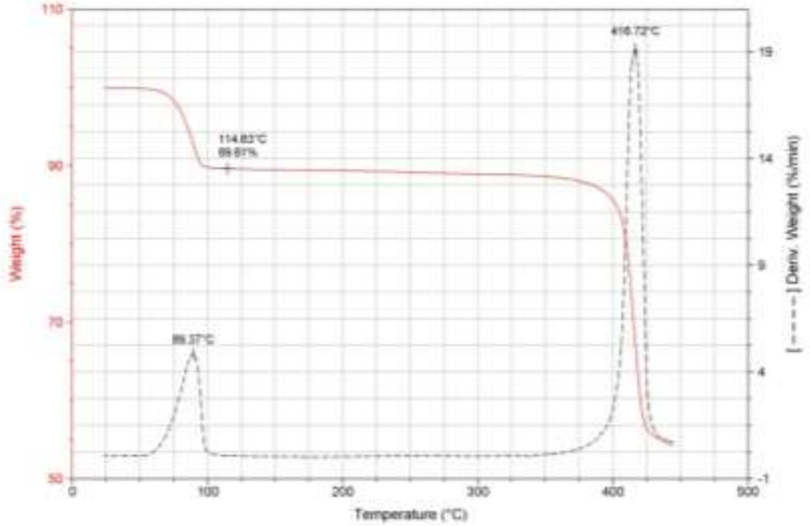


IR (ATR) spectrum of MgBA$_2$.

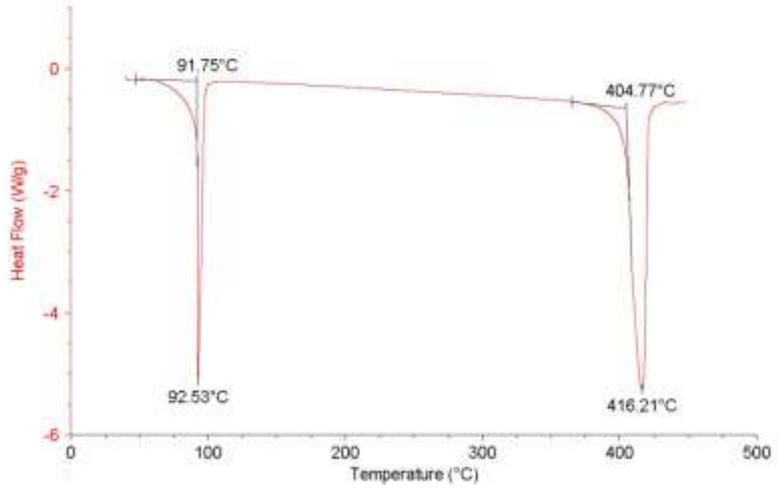


IR (ATR) spectrum of $CaBA_2 \cdot 3H_2O$.

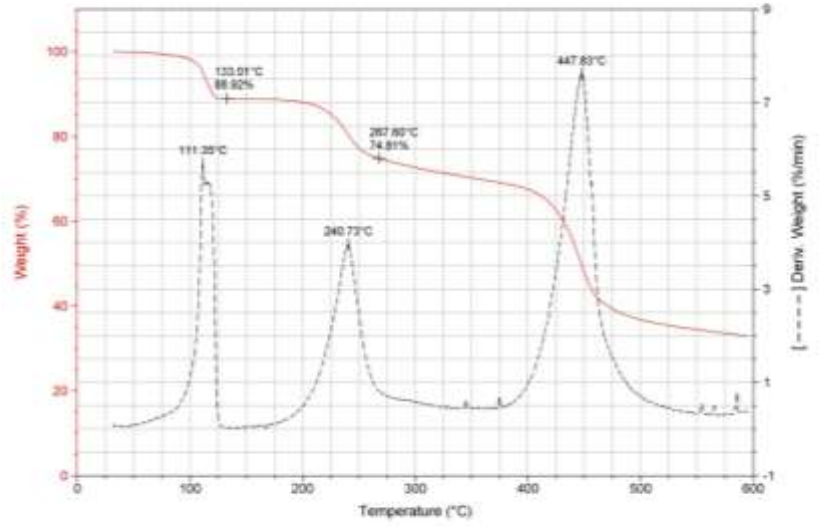
**Figures S4:** Calorimetric and Thermogravimetric curves of all prepared compounds.



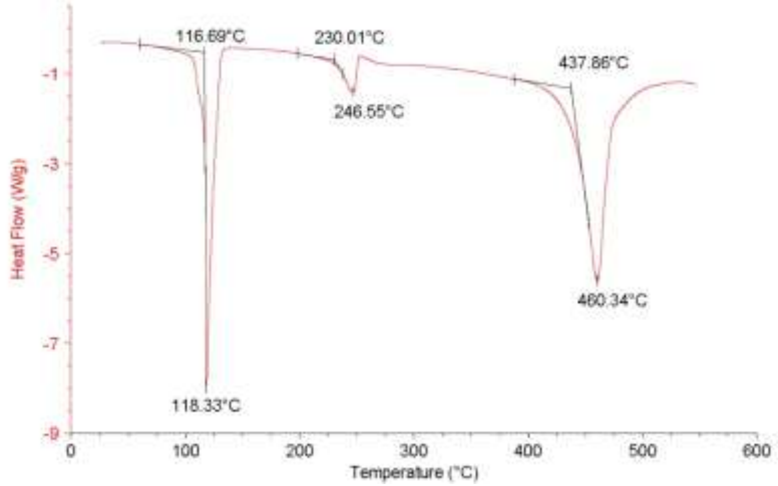
TGA curve of $NaBA \cdot 1H_2O$.



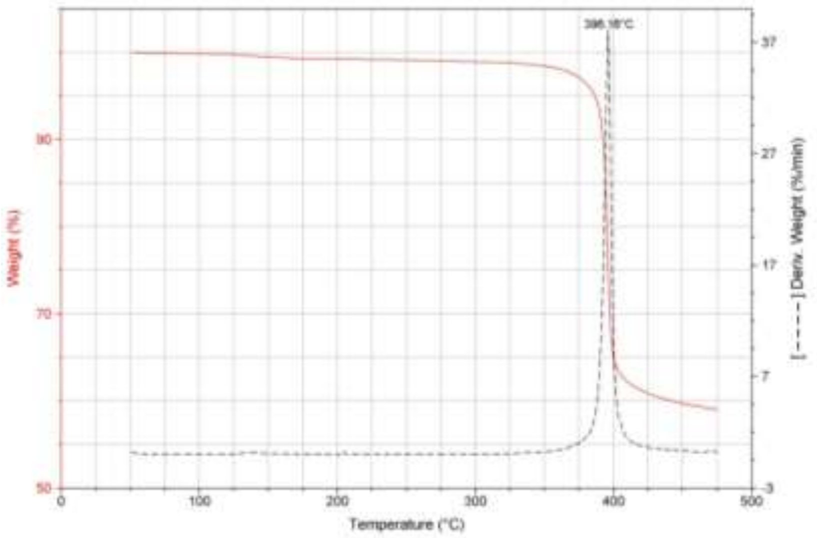
DSC curve of NaBA·1$H_2O$ (sealed pan).



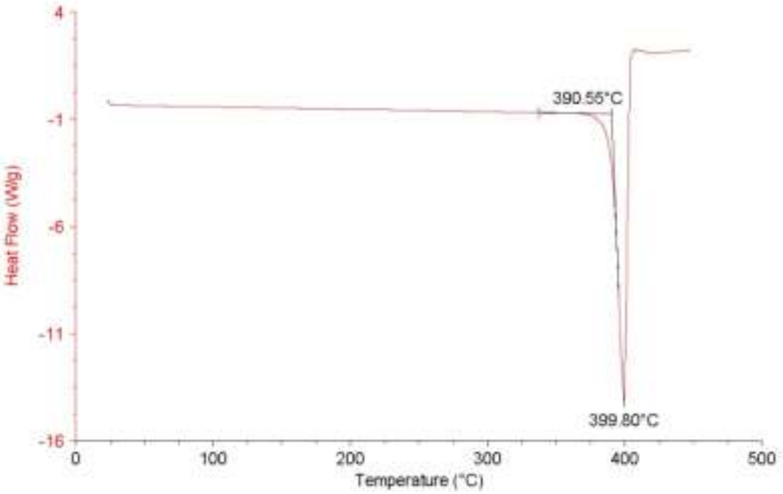
TGA curve of NaBA·HBA·2$H_2O$.



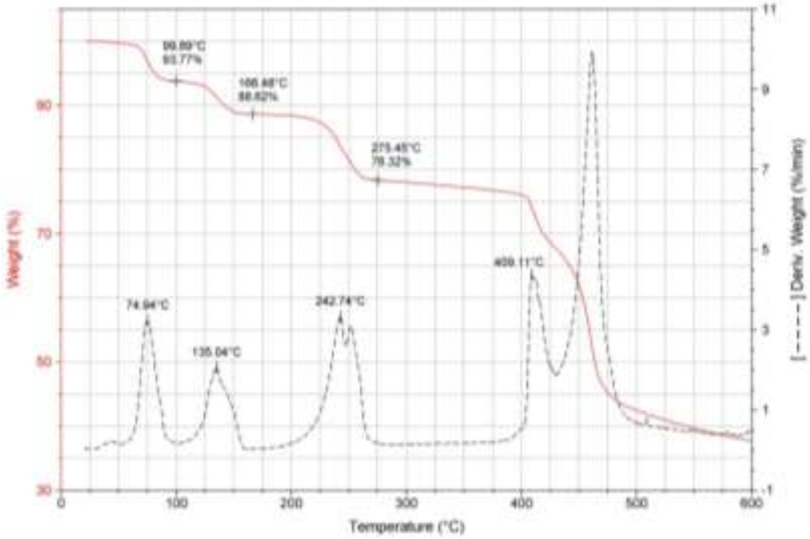
DSC curve of NaBA·HBA·2$H_2O$ (sealed pan).



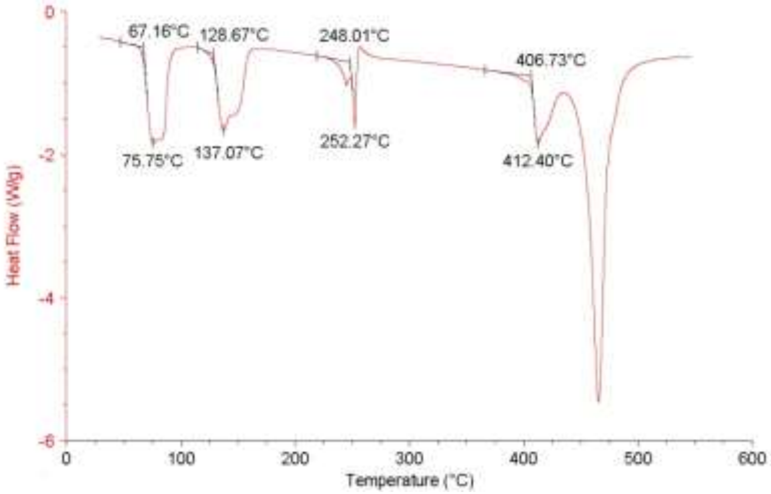
TGA curve of KBA.



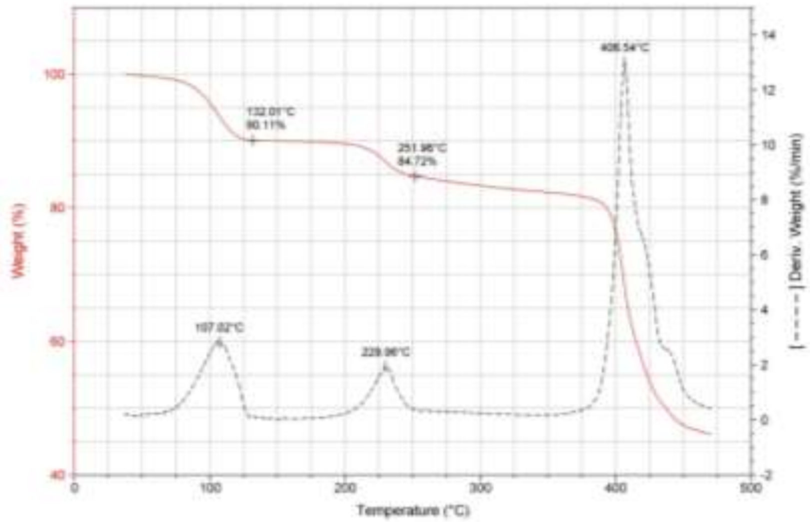
DSC curve of KBA (sealed pan).



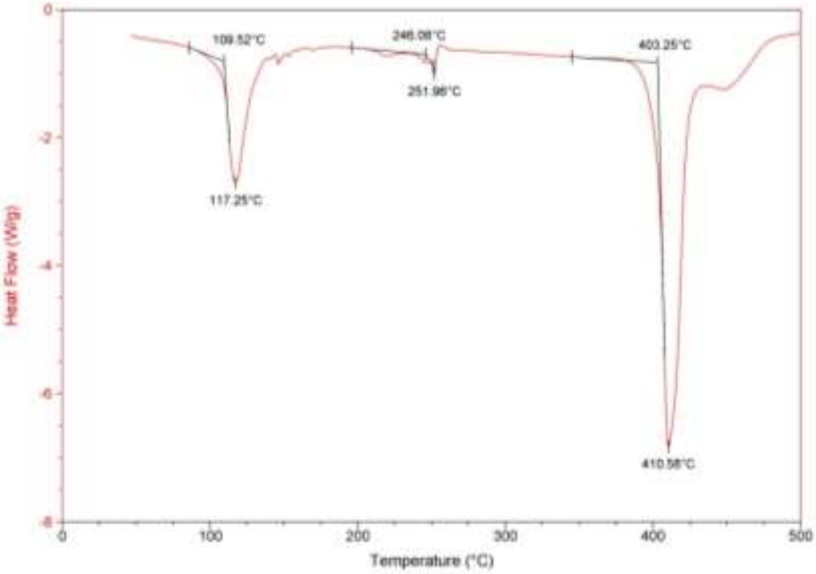
TGA curve of KBA·HBA·$2H_2O$.



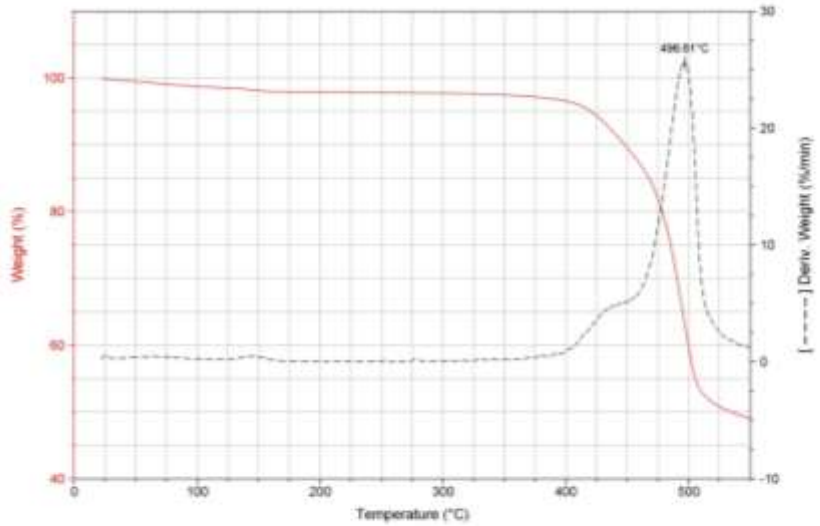
DSC curve of KBA·HBA·$2H_2O$ (sealed pan).



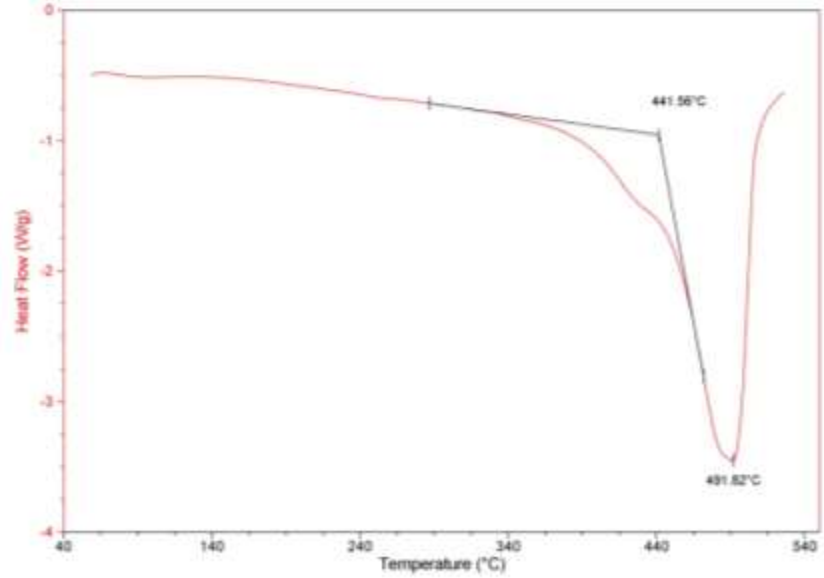
TGA curve of KBA·HBA$_{0.5}$·1.5H$_2$O.



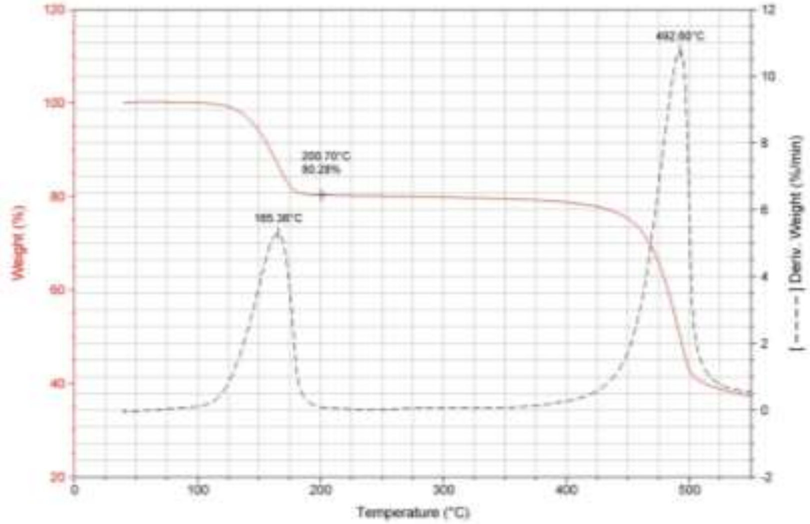
DSC curve of KBA·HBA$_{0.5}$·1.5H$_2$O (sealed pan).



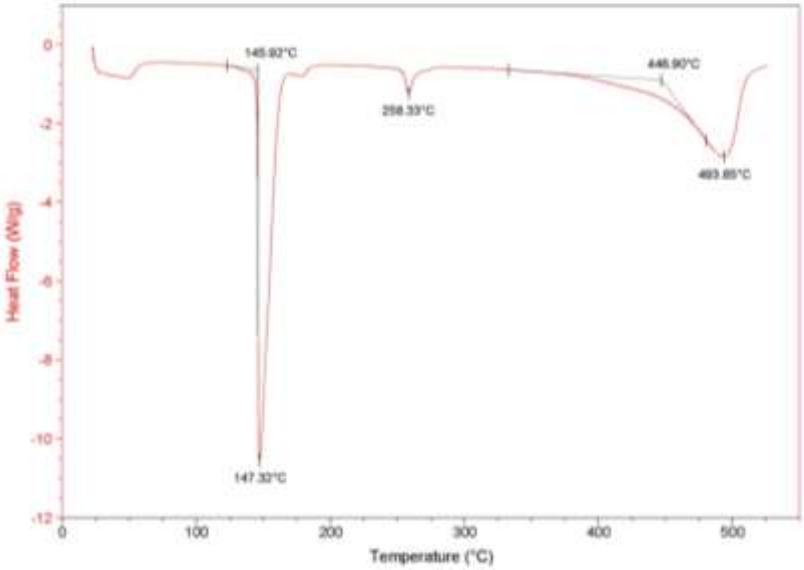
TGA curve of $MgBA_2$.



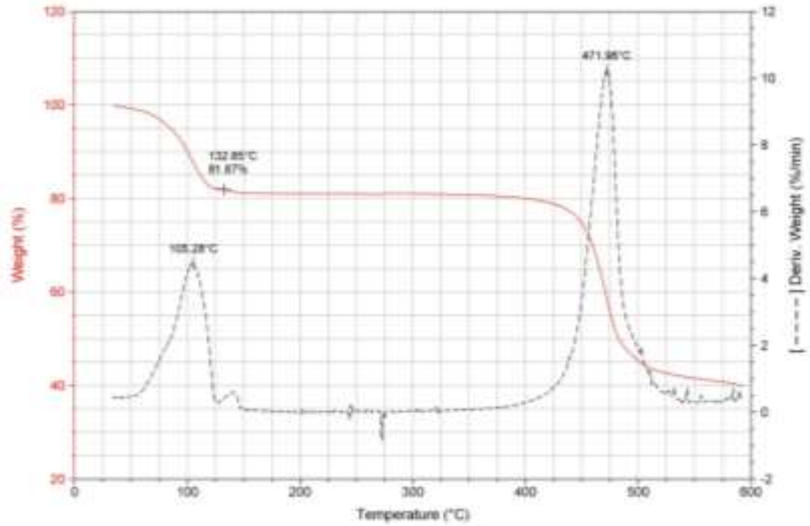
DSC curve of $MgBA_2$ (sealed pan).



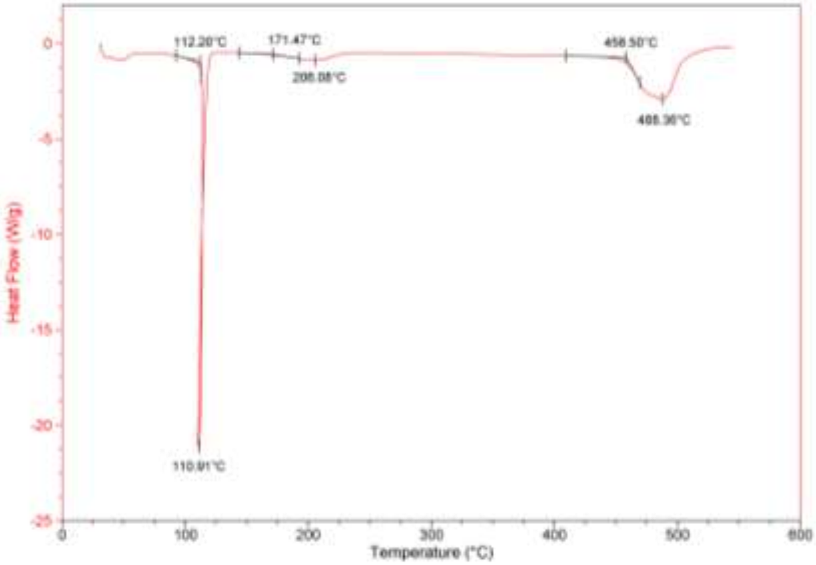
TGA curve of $MgBA_2 \cdot 2H_2O$



DSC curve of $MgBA \cdot 2H_2O$ (sealed pan).



TGA curve of $CaBA_2 \cdot 3H_2O$



DSC curve of $CaBA \cdot 3H_2O$ (sealed pan).