

# Four-component substitutional solid solutions of metal-organic frameworks with rare earth metal ions

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## INTRODUCTION & AIM

Multicomponent metal-organic frameworks (MOFs), which consist of 4 or more cations connected by an organic linker, can be classified as high-entropy materials (HEMs) when a “cocktail” effect, distortion of the local and/or atomic structure, slow diffusion, high entropy of mixing, and high concentration of valence electrons occur. As a result, the manifestation of a sudden increase in the characteristics of properties (but not all!) compared to single-component analogs is observed.

The aim of this work is to synthesize and characterize new multicomponent MOFs, obtained by the hydrothermal method by mixing salts  $RE^{3+}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$  ( $RE = \text{La-Lu}$ ) (in an equimolar ratio),  $\text{H}_3\text{BTC}$  (benzene-1,3,5-tricarboxylic acid) and  $\text{NaOH}$  in distilled water.

## X-RAY POWDER DIFFRACTION (XRPD)

(PowDiX 600;  $\text{CuK}\alpha 1$ ; Ni-filter;  $2\theta = 5\text{--}30^\circ$ )

➤  $RE^{3+} = \text{La-Pr}$  – single-phase;  $[(4RE)\text{BTC}(\text{H}_2\text{O})_6]$ ;

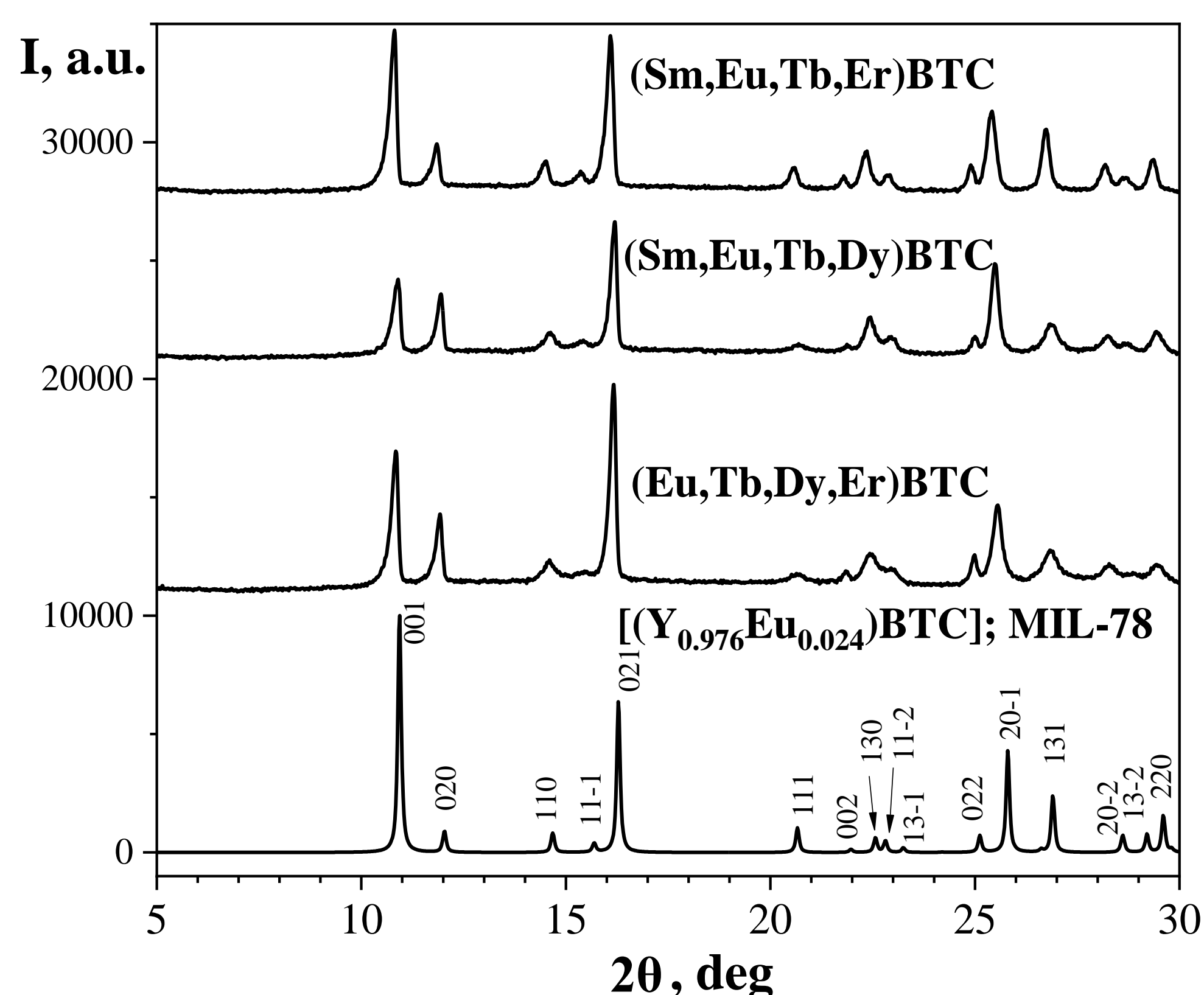
*Structure*:  $\text{REBTC}(\text{Cc})$ -type; space group  $\text{Cc}$ ,  $Z = 4$ ;

➤  $RE^{3+} = \text{Sm-Lu}$  – single-phase;  $[(4RE)\text{BTC}]$ ;

*Structure*: MIL-78-type; space group  $\text{C}2/m$ ,  $Z = 8$ ;

➤  $RE^{3+} = \text{Nd}$  – two-phase;

*Structure*:  $\text{REBTC}(\text{Cc})$ -type + MIL-78-type



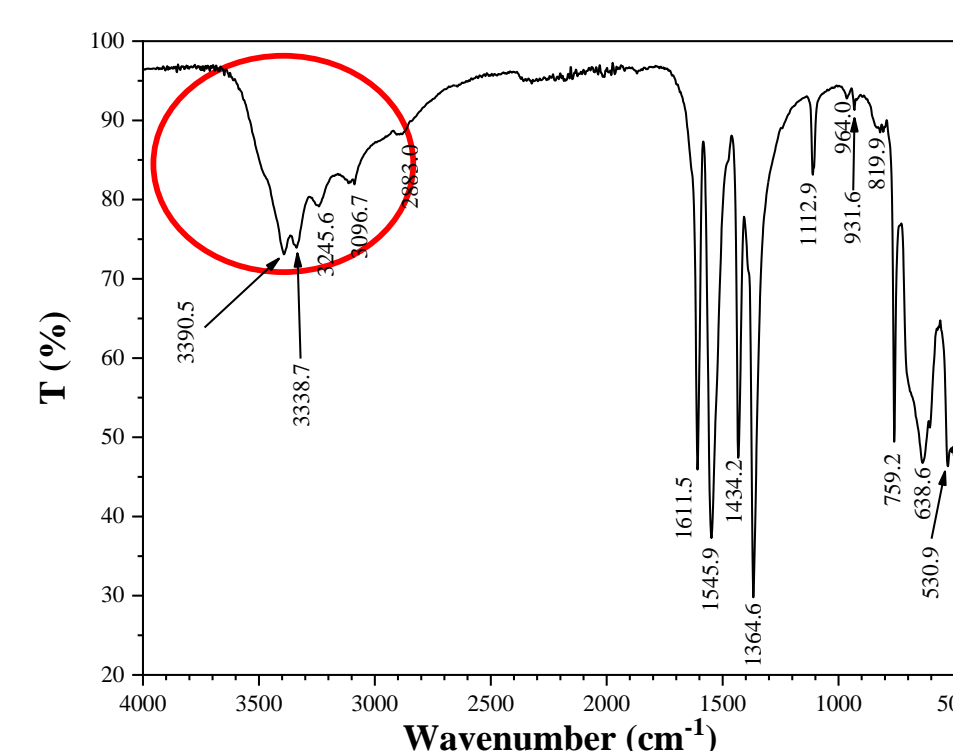
In the diffraction patterns of  $(4RE)\text{BTC}$  samples, the redistribution of intensities of main peaks is observed, which is caused by the type and content of  $RE$  in  $(4RE)\text{BTC}$

## IR SPECTROSCOPY

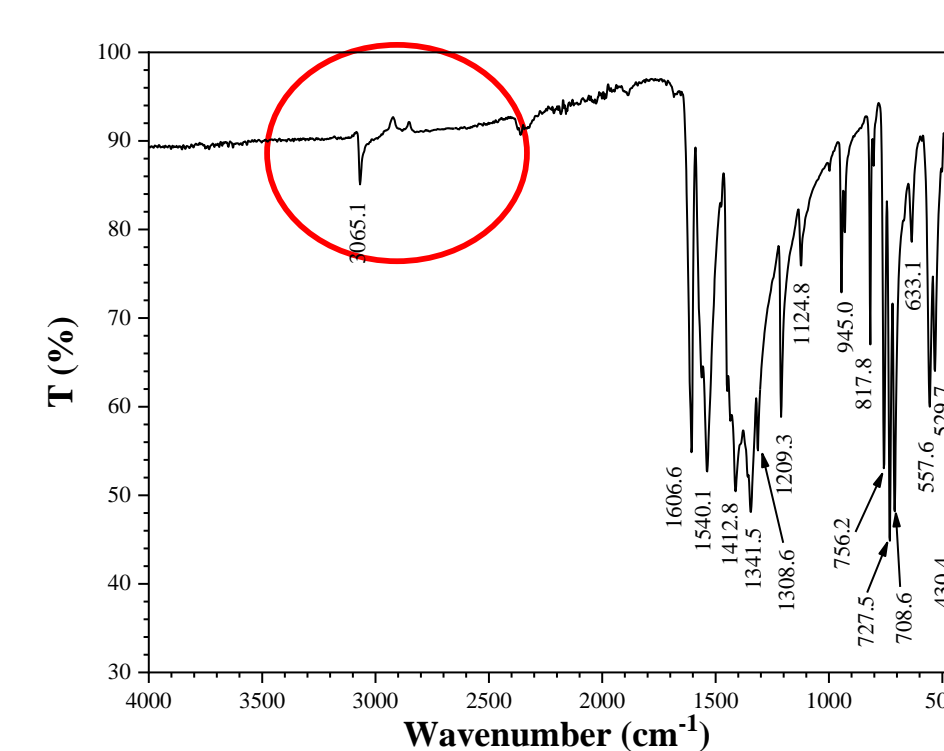
(WQF-530A,  $k = 350\text{--}4000\text{ cm}^{-1}$ )

IR spectra of  $[(4RE)\text{BTC}]$  and  $[(4RE)\text{BTC}(\text{H}_2\text{O})_6]$  confirm their compositions.

$[(4RE)\text{BTC}(\text{H}_2\text{O})_6]$



$[(4RE)\text{BTC}]$



Bands at  $\sim 3480\text{--}\sim 3230\text{ cm}^{-1}$  –  
*water in the framework*

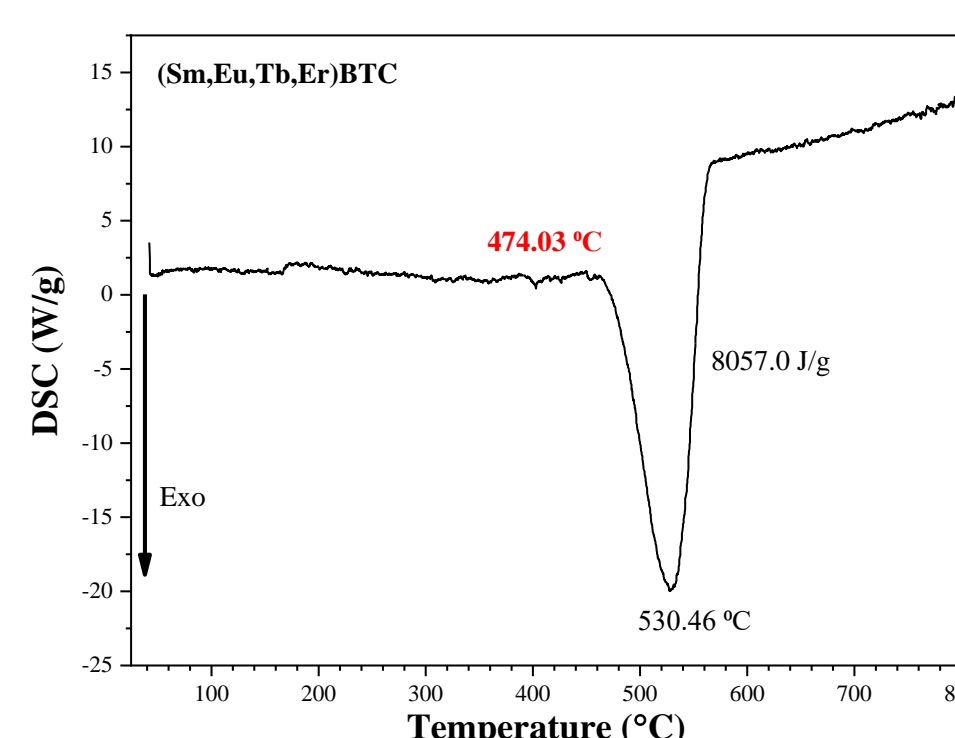
Band at  $\sim 3070\text{ cm}^{-1}$  –  
*adsorbed water*

## DIFFERENTIAL SCANNING CALORIMETRY (DSC)

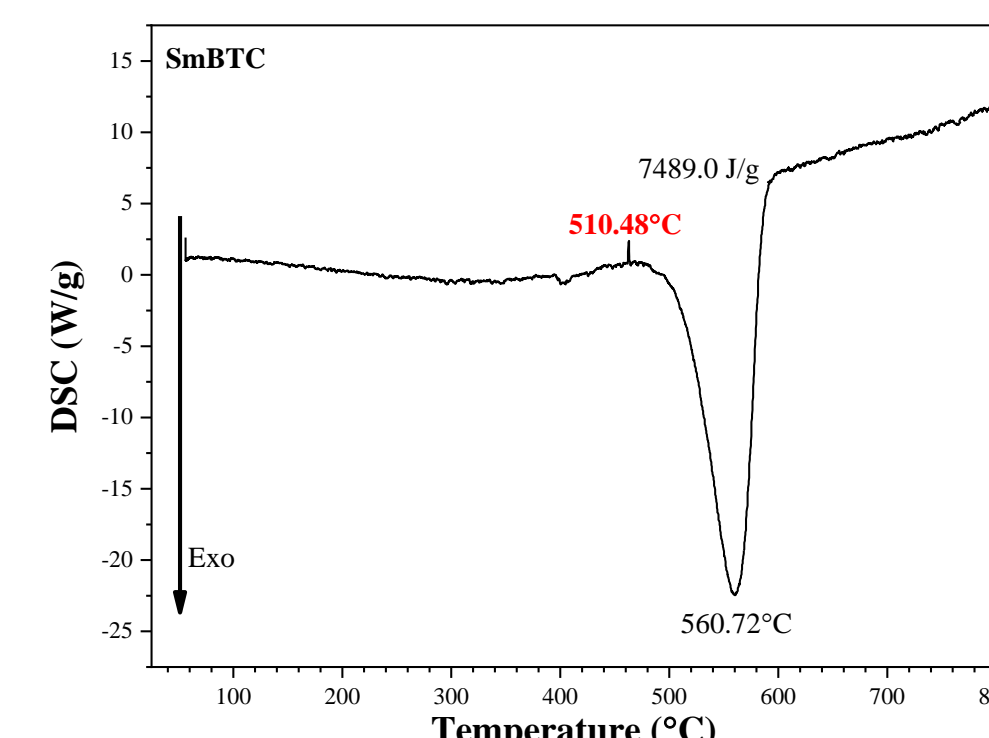
(ZCR-A; air; flow rate, 60 ml/min; scanning rate,  $10^\circ\text{C/min}$ )

The  $(\text{Sm},\text{Eu},\text{Tb},\text{Er})\text{BTC}$  has the highest chemical stability, greater than that of its components.

However, the highest thermal stability ( $560.72^\circ\text{C}$ ) is observed in the  $\text{SmBTC}$  component of  $(\text{Sm},\text{Eu},\text{Tb},\text{Dy})\text{BTC}$  and  $(\text{Sm},\text{Eu},\text{Tb},\text{Er})\text{BTC}$ , which may be due to a higher degree of amorphism in multicomponent phases compared to single-component ones.



Increased chemical stability in  
 $(\text{Sm},\text{Eu},\text{Tb},\text{Er})\text{BTC}$  ( $\Delta H_{\text{max}} =$   
 $8057\text{ J/g}$ ) compared to  $\text{REBTC}$ .



Exoeffect at  $560.49^\circ\text{C}$   
 $\Delta H = 7608.7\text{ J/g}$

## CONCLUSION

Four-component multicomponent MOF of a MIL-78 type with the general composition  $(4RE)\text{BTC}$  with rare earth metal ions ( $RE^{3+} = \text{Sm} - \text{Lu}$ ) and a benzene-1,3,5-tricarboxylic acid linker, firstly synthesized by the hydrothermal method, have increased chemical stability compared to single-component  $\text{REBTC}$ .

## FUNDING

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