

Supplementary Information

A cubic room temperature polymorph of thermoelectric TAGS-85

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1. Chemical composition analysis of as-prepared sample

Table S1. Chemical composition (and standard deviations in brackets) determined by EDS (Exp.) compared to nominal values (Calc.) for as-synthesized C_{RT} phase of TAGS-85. Values are averaged over 10 measurements.

Phase	Ge atomic %		Te atomic %		Sb atomic %		Ag atomic %	
	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
C _{RT}	37.0	36.2(0.9)	50.0	50.2(0.6)	6.5	6.2(0.6)	6.5	7.5(0.5)

2. Effect on crystal structure of holding time at 500 °C during initial cooling

The effect of different holding times at 500 °C during the initial cooling down process was studied. Portions of the X-ray diffraction patterns of some of the products obtained are shown in Fig. S1. The C_{RT} phase can only be obtained on quenching after holding for 3 h, as evidenced by the single 220 peak at $2\theta = 42.8^\circ$. Holding for a shorter time gives an inhomogeneous product with an average rhombohedral structure, for which the cubic 220

peak is split into a doublet indexed as 211 ($2\theta = 42.3^\circ$) and 10Error! ($2\theta = 42.9^\circ$). Holding for longer than 3 h leads to progressively sharper rhombohedral peaks; annealing for at least 20 h is necessary to obtain a good quality sample.

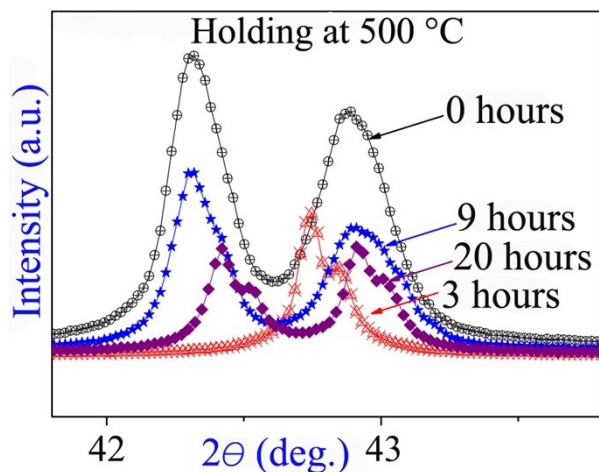


Figure S1. Partial room temperature XRD patterns showing the effect of holding time at 500 °C for 0, 3, 9 and 20 h during initial cooling down procedure.

3. Fitted X-ray diffraction pattern of as-synthesized C_{RT} sample

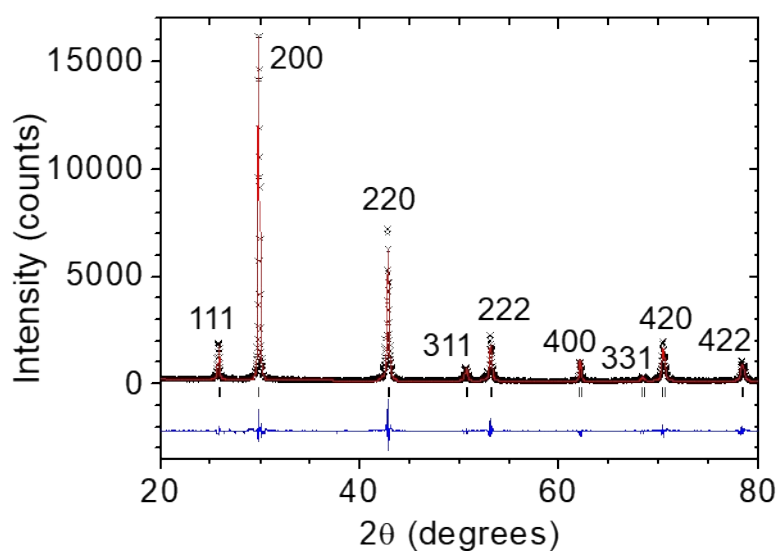


Figure S2. Observed (black data points), calculated (red line) and difference (blue line) XRD profiles of as-synthesized C_{RT} sample.

4. SAED measurements of C_{RT} phase

In an attempt to confirm whether a local rhombohedral distortion is present in the C_{RT} sample, and to investigate whether the sample preparation method might affect the structure, a number of further SAED patterns were collected on a second C_{RT} sample prepared for TEM measurements using the FIB technique (the sample measured in Fig. 1 was prepared using the ion milling technique). Figure S3 shows SAED patterns taken on the second sample along four different zone axes, [112], [011], [123] and [213]. The patterns appear to be fully consistent with cubic symmetry; there is no obvious spot splitting and the observed systematic absences (hkl , all indices odd or even) are consistent with the $Fm\bar{3}m$ space group. However, it should be noted that more extensive electron diffraction measurements are required to prove or disprove the presence of a rhombohedral distortion with certainty.^[1] Therefore, more research is required to understand the true nature of the C_{RT} phase.

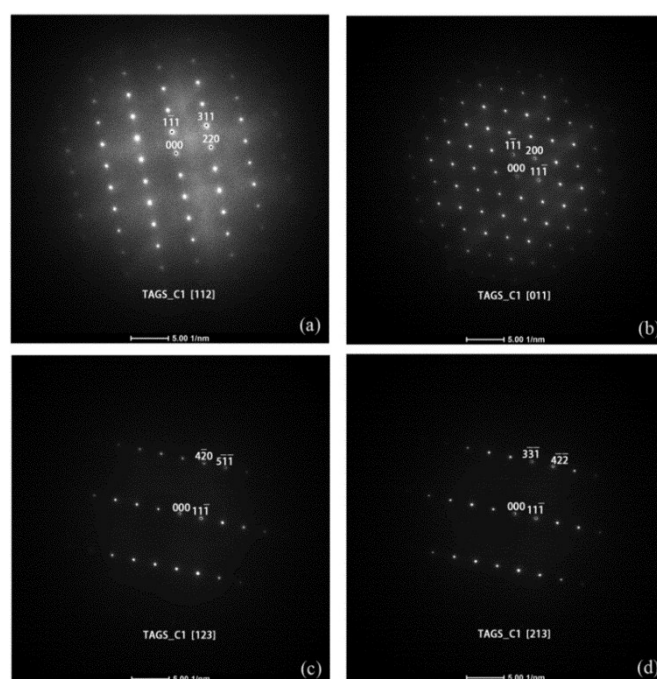


Figure S3. Selected area electron diffraction patterns taken on a C_{RT} sample along four different zone axes: a) [112], b) [011], c) [123], d) [213].

5. TGA/DSC measurements on C_{RT} sample

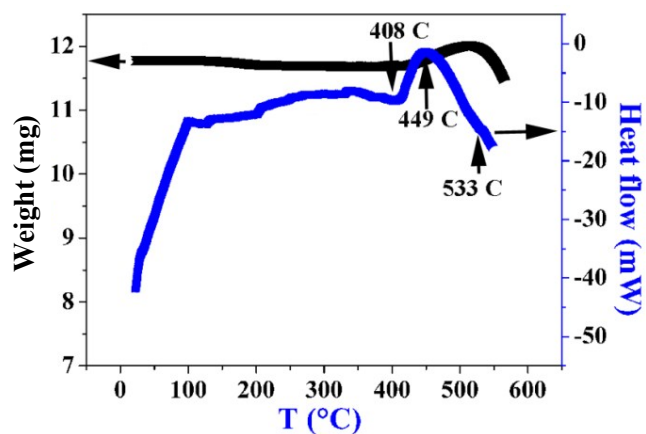


Figure S4. TGA (black curve) and DSC (blue curve) measurements on as-synthesized C_{RT} phase heated in an argon atmosphere.

Reference

[1] P. A. Vermeulen, A. Kumar, G. H. ten Brink, G. R. Blake and B. J. Kooi, *Cryst. Growth Des.* 2016, **16**, 5915.