

Supplementary materials:

## **Ionic cross-linked polyvinyl alcohol tune vitrification and cold-crystallization of sugar alcohol for long-term thermal energy storage**

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Figure S2. DSC curves of CC-PCM (a) compositions C, C1, and C2 under 5 K/min scan rate; (b) heating-cooling cycles of different CC-PCM compositions under 0.5 K/min slow scan rate.

Figure S3. Micrographs of CC-PCM (composition A) on cooling from molten state at 120 °C to deeply supercooled state and cold-crystallization on reheating. Note the spheres in the micrographs of molten state are air bobbles appeared during sample preparation between the glass slides and cover glass.

Figure S4. Specific heat capacity ( $C_p$ ) of CC-PCM: compositions (a) B, B1, and B2, (b) C, C1, and C2 and (c) PVA and ERY by temperature under 5 K/min scan rate on heating (phase transition regions are not included for simplicity). Note that PVA exists only in solid form in the measured temperature range and ERY exists in both liquid and solid form as marked in the graph.

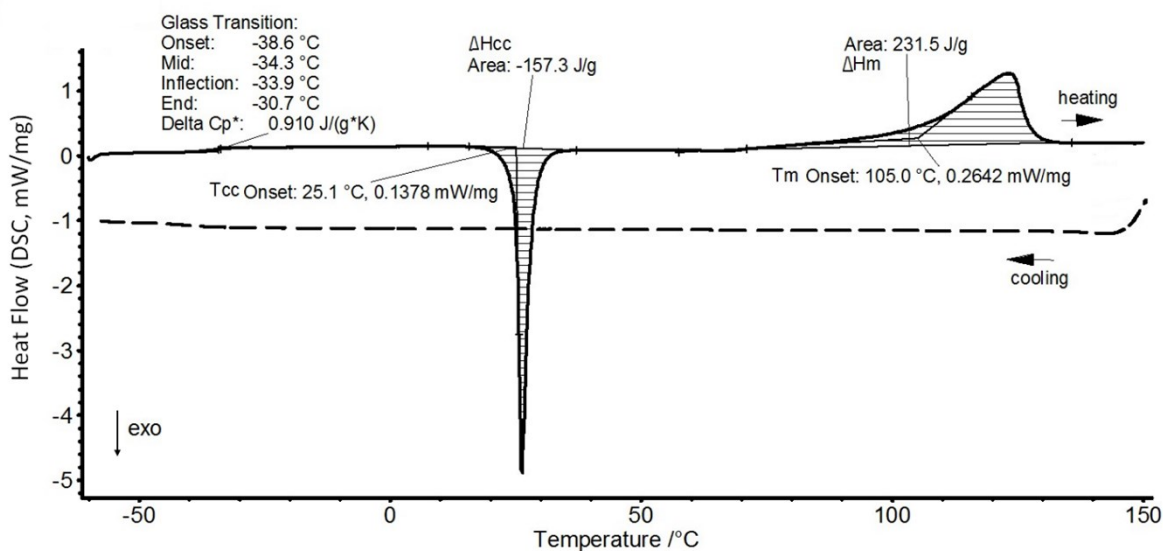
Figure S5. Specific heat capacity ( $C_p$ ) of CC-PCM on cooling with 5 K/min scan rate (a) compositions with lower SC (b) compositions with higher SC: demonstration of readily vitrification.

Figure S6. The difference plot of rietveld refinement of the high resolution XRD pattern of CC-PCM (C2) (in red) and the calculated powder diffractogram of the single erythritol crystal (in blue with peak position in green) by Ceccarelli et al. <sup>4</sup>.

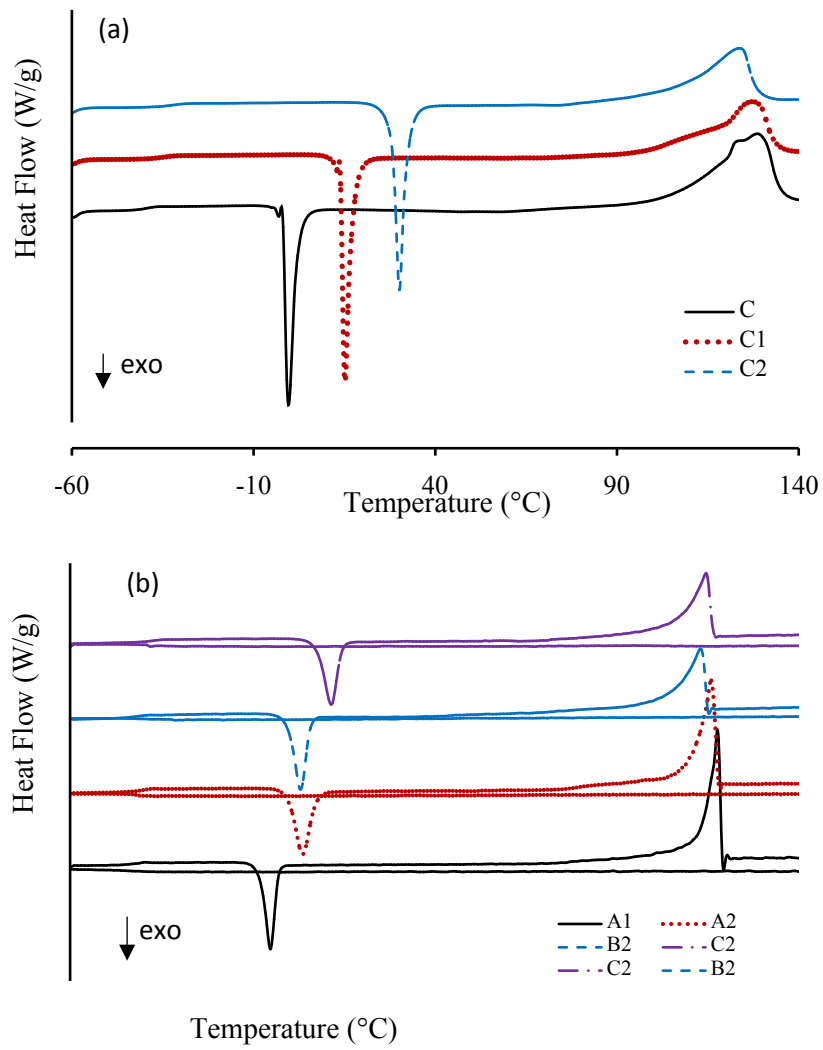
Figure S7. DSC curves of CC-PCM (B2) under 5 K/min heating-cooling scan rate (a) stability test of supercooled state (between -40 °C and 15°C) and (b) effect of cooling end temperature on cold-crystallization.

### Differential Scanning Calorimetry (DSC) Methodology:

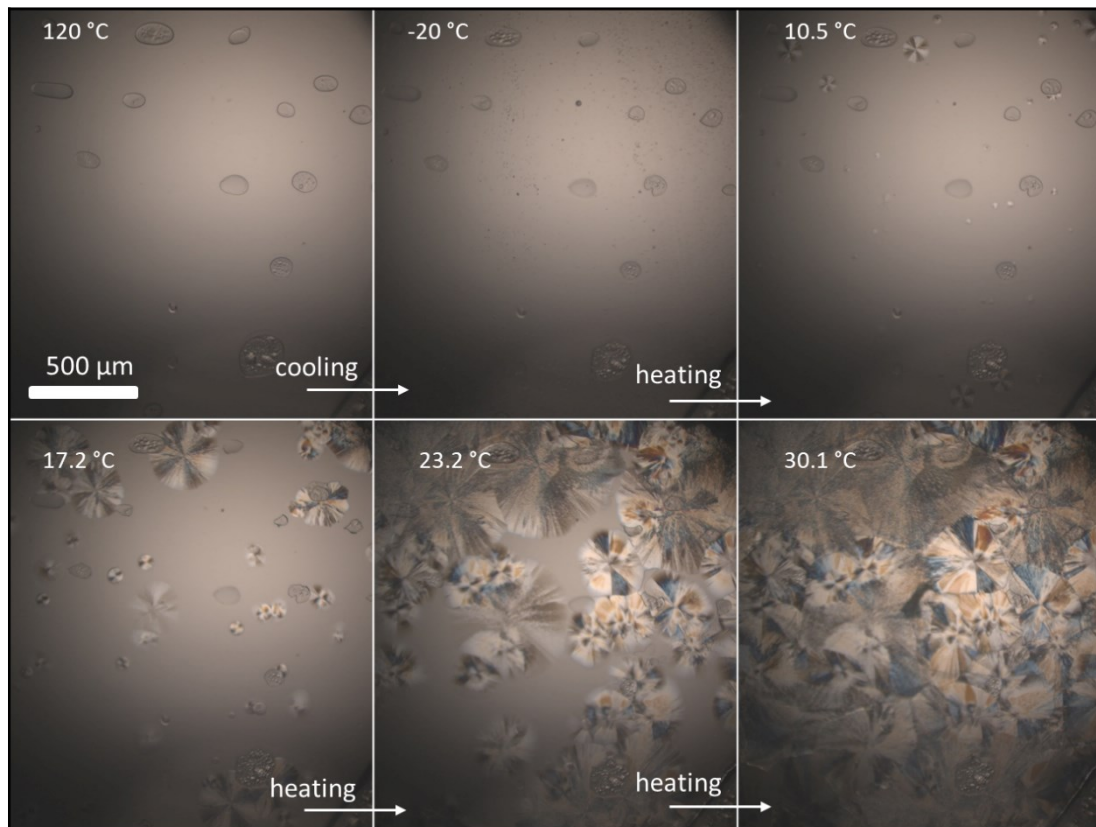
Differential scanning calorimetry (DSC) is the most common standard method used to determine the latent heat (enthalpy) of crystallization and melting and corresponding phase transition temperatures of phase change materials (PCMs).<sup>1</sup> DSC measures the difference of heat flow rate in a sample PCM and a reference (usually alumina) as a function of the temperature, when both the sample and the reference are exposed to the same DSC heating-cooling program.<sup>2</sup> An exothermic crystallization reaction in the sample causes a heat flow out of the sample, while, the heat flows into the sample by an endothermic melting reaction. Based on the developed temperature differences between the sample and the reference, DSC measures the heat flow as the plot of the heat flow versus temperature (DSC curve). Latent heat (enthalpy) of the phase change (crystallization and melting) is determined as the area under the exothermic and endothermic peaks on the DSC curve, respectively. The phase transition temperatures are assigned to the onset of the peaks determined by line fitting.<sup>1-3</sup> An example DSC curve and corresponding phase change measurements are illustrated in Figure S1. For instance, the latent heat of cold-crystallization and melting for the sample B2 are  $\Delta H_{cc} = -157 \text{ J/g}$  and  $\Delta H_m = 231 \text{ J/g}$ , respectively. Table 2 in the article reports the measured latent heat storage properties for the rest of the compositions.



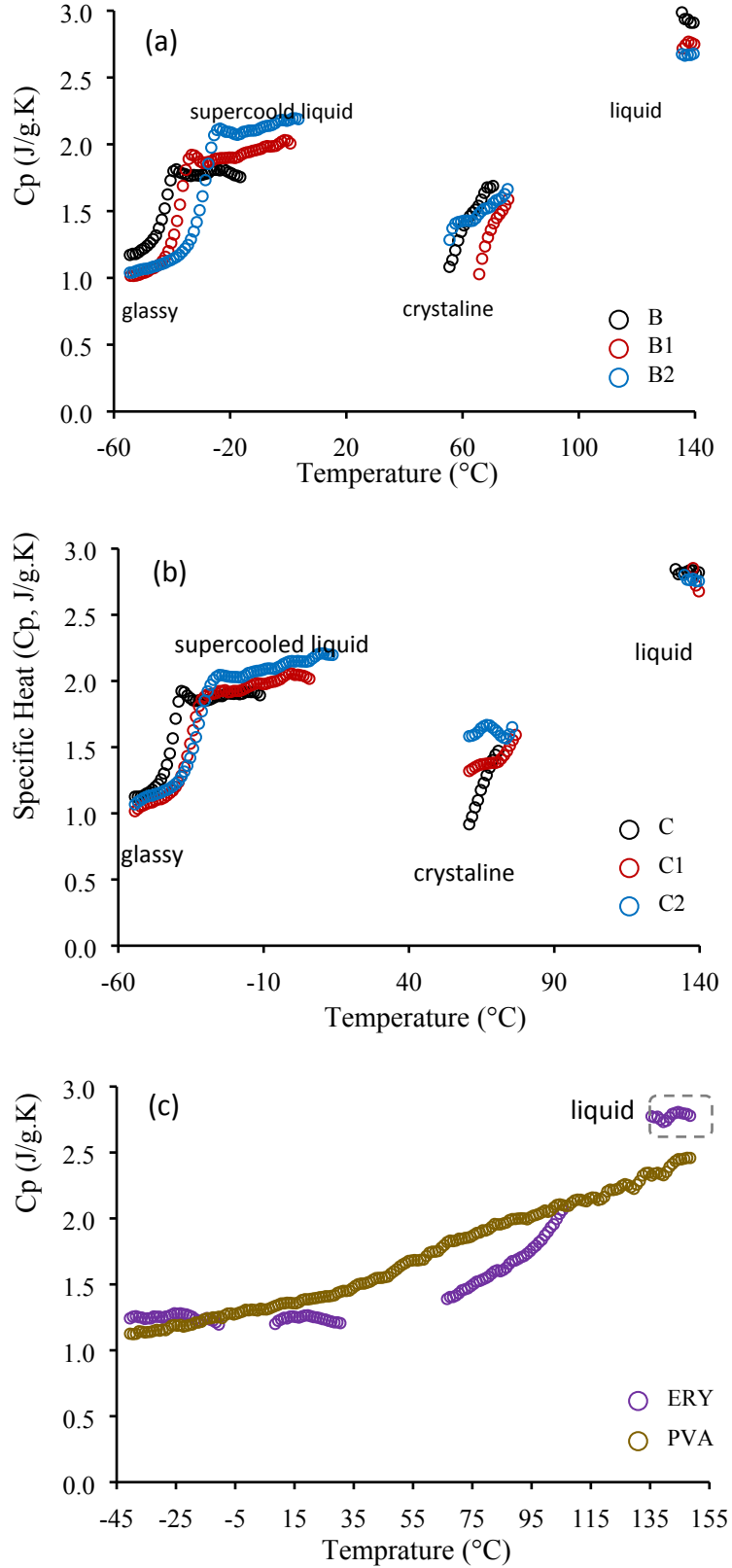
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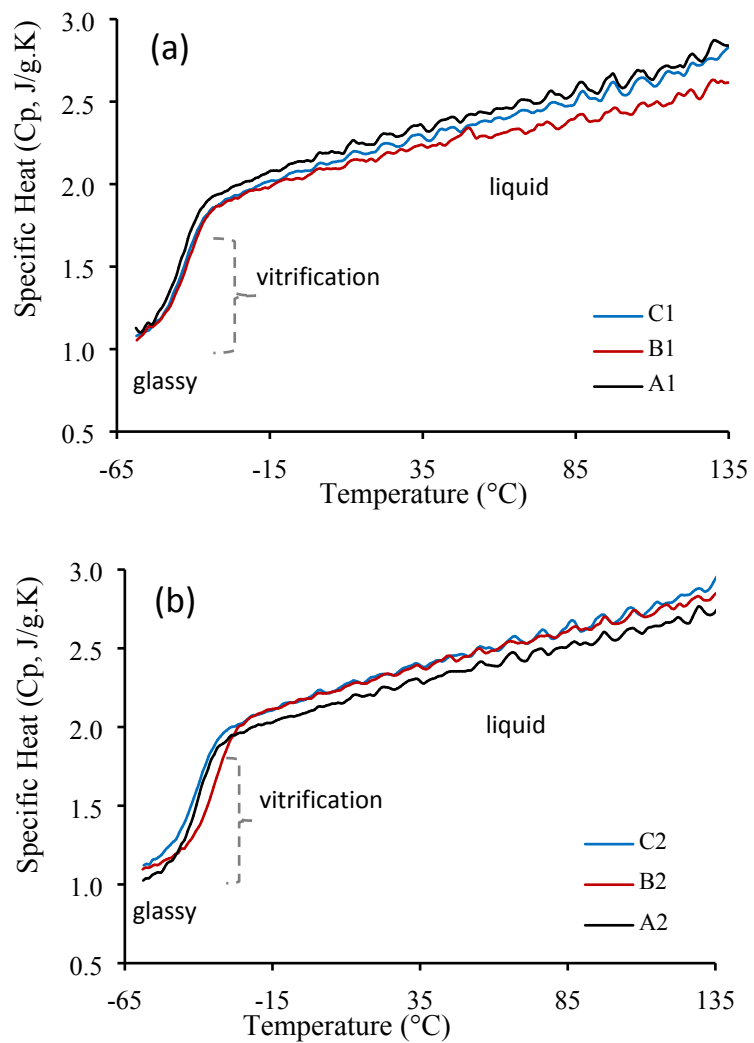
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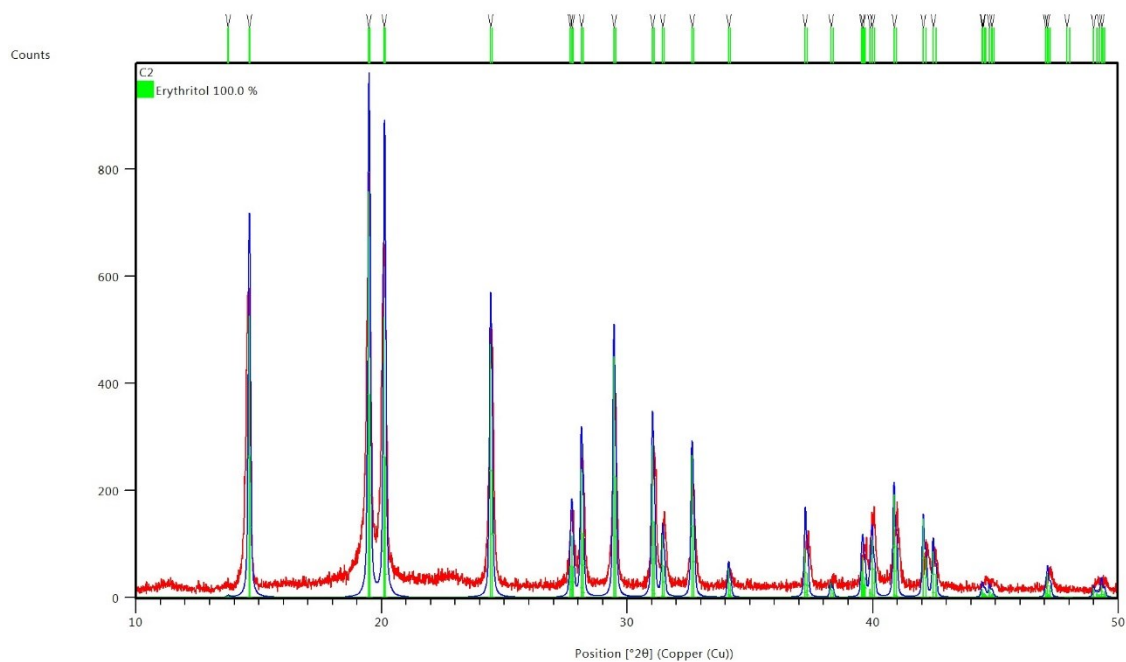
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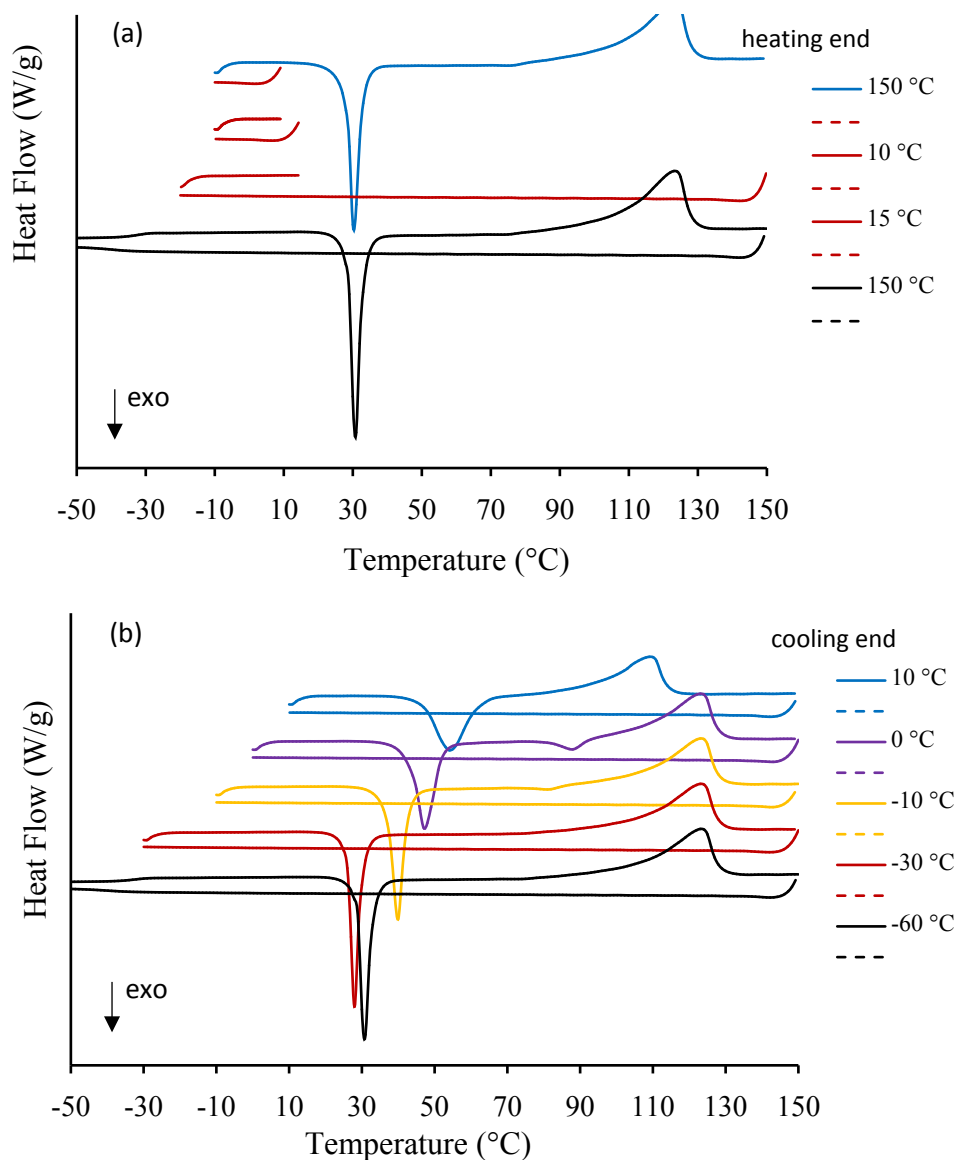
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## References

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