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The Experimental Phase Diagram Study of the Binary Polyols System Erythritol-Xylitol

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Abstract

A comprehensive phase diagram for the binary polyols system erythritol-xylitol has been mapped with a transparent characterization approach. Here, the phase equilibrium of the system has been studied experimentally using a combination of methods: Temperature-history (T-history), X-Ray Diffraction (XRD), and Field-Emission Scanning Electron Microscopy (FESEM), and linked to Tammann plots. Existing literature has previously shown the system to be a non-isomorphous type forming a simple eutectic, by combining experimental data with theoretical modelling. The present investigation shows that the system's phase diagram is a partially isomorphous type forming a eutectic, but not a non-isomorphous type forming a simple eutectic. Here, the eutectic was found within 25-30 mol% erythritol and at 77 °C, which differs from the previous studies identifying the eutectic respectively at 25 or 36 mol% erythritol and at 82 °C. The reasons for the differences are hard to deduce since the research approach is not presented as fully transparent from the past studies. In the present study, only the temperature-composition plot of the first melting (of the two components in a physical mix, but not of a single blend) indicated the shape of a simple eutectic in a non-isomorphous system. The cycles after the first melting in contrast started from the real blend, and displayed eutectic and solid-solid phase changes in T-history. These were verified as forming solid solutions with XRD and FESEM. This eutectic melts at a temperature suitable for low-temperature solar heating, but displayed glass transition, supercooling, and thermally activated degradation, thus affecting its practical aspects as a PCM.

Keywords: Phase change material (PCM); Erythritol-Xylitol phase diagram; Temperature-history (T-history) method; X-ray diffraction (XRD); Field-emission scanning electron microscopy (FESEM); Eutectic

Nomenclature

Symbols

A	Heat transfer area (m ²)
c_p	Specific heat at constant pressure (kJ/(kg·K))
Δh	Enthalpy change (kJ/kg or kJ/mol)
dT	Temperature difference (K, °C)
Δt	Time difference (s)
k_1	Constant (W/K)
k_2	Constant (W)

Imtd	Logarithmic mean temperature difference (K)
m	Mass (g)
Q	Heat (J)
$\dot{Q}$	Heat transfer rate (W)
SSTT	Stainless steel test tube
t	Time (s)
T	Temperature (°C)
U	Overall heat transfer coefficient (W/(m ² ·K))

Subscripts and superscripts

E	eutectic
M	melting
SS	stainless steel
S-S	solid-solid
Intm	intermediate
Tot	total
R	reference

Abbreviations

Cu-ETP	electrolytic copper
DSC	Differential Scanning Calorimetry
DTA	Differential Thermal Analysis
Er	Erythritol
FESEM	Field-emission Scanning Electron Microscopy
FT-IR	Fourier Transform Infra-Red Spectroscopy
HT	High-temperature
HTXRD	High-temperature X-Ray Diffraction
IR	Infra-Red
IRT	Infra-Red thermography
L	liquidus
NA	Not available
NPG	Neopentyl glycol
PCM	Phase Change Material
PER	Pentaerythritol
PLM	Polarized Light (thermo-) Microscopy
PTFE	Polytetrafluoroethylene
RT	Room-temperature
RTD	Resistance Temperature Detectors
RTXRD	Room-temperature X-Ray Diffraction
S	solidus
SEM	Scanning Electron Microscopy
S _{Er}	a solid solution of erythritol
S-S	solid-solid / solvus (in the phase diagram)
S-SPC	solid-solid phase change
S _{Xy}	a solid solution of xylitol

TE	Trimethylol ethane
TEM	Transmission Electron Microscopy
TES	Thermal Energy Storage
TGA	Thermogravimetric Analysis
T-history	Temperature-history
TPS	Transient Plane Source
XRD	X-Ray Diffraction
Xy	Xylitol

1 Introduction

Energy storage is needed for the effective utilization and management of energy. In that, thermal energy storage (TES) is one alternative. TES enables load shifting of thermal energy demand ([1]-[4]), with opportunities for cost-benefits depending on the type of supply system. Also, TES can alleviate fossil fuel-based heating and cooling demands by storing excess thermal energy from industries and power plants (e.g. [5]-[10]), and thus mitigating CO₂ emissions ([11], [12]). Such stored heat or cold can balance the energy mismatch between these sources and demands at different locations and time (e.g. [13], [14], [15]-[17]). Phase change materials (PCMs) are attractive for TES, with a higher storage density as compared to sensible TES, and the ability to regulate temperatures within a narrow window. To integrate renewable energy sources, particularly such as solar heating and cooling, PCMs are an effective storage choice [18], [19]. The challenges in PCM design include cost, and accomplishing a material with robust functionality while avoiding issues like supercooling and phase separation. Material blends could be tailored as PCMs for specific applications. In addition, if the blends e.g. come as industrial by-products, those could prove to be cost-effective PCMs. However, blends come with complex phase changes. Here, a phase equilibrium study, including establishing the phase diagram, is the key to find compositions that have sharp, reversible¹ phase change and no phase separation (e.g. congruent melting compositions, and eutectics if no supercooling occurs [20]). In addition, compositions already known to supercool and phase separate can be avoided (e.g. peritectics [20]).

Polyols (or poly alcohols, i.e., alcohols containing more than one hydroxyl group) are attractive candidate PCMs (e.g. [21]-[35]), with low to moderate melting temperatures and considerable melting enthalpies (~-15 °C to 245 °C and 100-413 kJ/kg) [29], renewable origin, and non-toxic nature [29], [36]. Their material challenges include: glass transition (e.g. xylitol, sorbitol and maltitol [29], [37]-[40]); thermally activated degradation (i.e., browning and thickening [29] or tanning [34] in e.g. erythritol, xylitol, myo-inositol, galactitol and D-mannitol [13], [27], [29], [34], [41]); large supercooling (e.g. erythritol [29] and mannitol-galactitol [31]); and considerable hysteresis (e.g. myo-Inositol, galactitol, and D-mannitol [27]). Polyols are prone to metastabilities as well, which is also an important TES design fact. A predominant metastable solid-solid phase was reported e.g. for erythritol at 102-112 °C with an enthalpy of 255-314 kJ/kg [28], [29], [42], and for xylitol at 61-61.5 °C [43], [44] (and the enthalpy is unknown).

A number of polyol blends have also been studied assessing their phase equilibrium in the PCM-context ([21]-[23], [31], [38], [45]-[50]), including the erythritol-xylitol system ([21], [22], [33]). These have identified: numerous eutectics (in erythritol-xylitol, erythritol-sorbitol, sorbitol-xylitol, adonitol-

¹ i.e., a phase change (of e.g. solid-liquid change) that undergoes complete transformation for any number of cycles

erythritol, arabitol-erythritol, arabitol-xylitol, erythritol-dulcitol, xylitol-mannitol, adonitol-mannitol, and mannitol-dulcitol [21], [22], [31]- [33], [38], [47]- [49]); some monotectics (in D-sorbitol-D-mannitol, xylitol-dulcitol, xylitol-D-mannitol, and adonitol-dulcitol [38], [46]-[48]); and a co-crystalline behavior (in xylitol-D-sorbitol and sorbitol-mannitol [47]). Among certain polyols, miscibility gaps among components with dissimilar structures (e.g. Pentaerythritol (PER)-neopentyl glycol (NPG) and pentaglycerine (PG)-NPG) and solid solubility among polyols with similar crystal structures (e.g. PER-PG) have also been observed [46]. The ring-structured polyols (e.g. mannitol, dulcitol and inositol) were found to improve the thermal endurance of eutectic polyol blends involving them [32].

The focus in this paper is on the system erythritol-xylitol, raising hopes for suitable PCM-blends in the temperature range 60-120 °C which is highly relevant for (solar) heating applications. Recently, the phase diagram for this system was concluded to be containing a simple eutectic in a non-isomorphous system², based on phase equilibrium studies using a combination of methods (Differential Scanning Calorimetry (DSC) [21], [33], Infrared Thermography (IRT)³ [33], Polarized Light Microscopy (PLM), X-Ray Diffraction (XRD) [21], and thermodynamic modelling [21], [33]). However, in another study, the same system was analyzed experimentally employing the Temperature-history (T-history) method [22], which showed that in addition to a possible eutectic, solid-solid and other complex phase changes were present. It was then concluded that the thermal property evaluation alone was insufficient to explain these complexities as well as the disparities found between the studies.

Comparing these erythritol-xylitol investigations, some of the presented phase diagrams are preliminary, for lacking physical characterizations [22], [33], and for containing a wide dispersion in the liquidus points [33]. The final erythritol-xylitol phase diagram was concluded by evaluating, three chosen melting cycles (involving seeding during cooling) in the T-history study [22], or an unspecified number of cycles in the other studies [21], [33]. Diarce et al. [21] only detail the use of: one melting in DSC with no indication of seeding; and in PLM the first melting, a seeding induced freezing, and another melting [21]. There, the PLM was used to justify the use of the offset temperature of the DSC specific heat (c_p) melting peak as the liquidus, and to determine a slow heating/cooling rate to maintain thermal equilibrium [21]. The DSC was used to find the liquidus of the system using the slow rate defined by PLM [21]. With no new or disappearing peaks observed in XRD at room temperature, the system was concluded to be immiscible in the solid-state, which was then used as a condition in the theoretical modelling [21]. Del Barrio et al. [33] derived their phase diagrams primarily using the IRT method, and simplified theoretical modelling assuming ideal liquid solutions. They ([33]) only detail: melting the powders externally and pouring a droplet of this into the IRT plate cavities; cooling the droplet at room temperature till crystallization; and evaluating the melting of this solid in the IRT. The DSC was only used to 'refine' the eutectic by examining the thermograms around its composition, and to determine the melting enthalpies of the pure components and the blends [23], [33]. There, for the samples tested in the DSC, only the first melting was detailed [23].

Given these procedural and results inconsistencies in literature, with the main objectives of comprehensively determining the erythritol-xylitol phase diagram, and to explain the complexities observed, this paper presents an experimental phase equilibrium analysis of the erythritol-xylitol system.

² i.e., a non-isomorphous system (a system completely immiscible at the solid state) with just a single eutectic.

³ In the IRT method, blend droplets deposited on small cavities on an aluminum plate mounted on a heating/cooling stage are imaged using an IR camera, after which the IR emissivity changes during heating are mathematically interpreted to estimate the phase change temperatures [23].

For that, a combination of experimental methods have been used: the T-history method (coupled with a Tammann plot assessment); X-Ray Diffraction (XRD); and Field-Emission Scanning Electron Microscopy (FESEM). Here, including the cycled behavior of the system for at least three cycles was also prioritized. The thermal conductivity of the pure components and some blends are also presented, determined using the Transient Plane Source (TPS) method with a Hot Disk Analyzer.

2 Experimental Investigation: Materials and Methods

So far, polyols have been studied using the experimental methods: DSC ([13], [21], [28], [33], [38]-[40], [42], [45], [47], [51]-[56]); T-history ([22], [28], [29]); Differential Thermal Analysis (DTA) ([13], [54]); other calorimetric methods ([52], [54], [56]-[58]); Thermogravimetric Analysis (TGA) ([13], [31], [47]); IRT ([23], [33]); XRD ([21], [31], [45]-[47]); FT-IR ([27], [31], [51], [59]); PLM [21]; and optical microscopy [34]. DSC, T-history, DTA, TGA, IRT and calorimetric methods characterize the thermal properties of materials, whereas XRD, FT-IR, PLM, and optical and other microscopic techniques characterize their physicochemical properties. In PCM design with blends, it has so far been very common to only pay attention to thermal properties [20]. However, the physicochemical aspects are essential to confirm the thermal property-based phase change identifications. Microscopy methods like Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) can also effectively complement phase equilibrium evaluations ([60]-[65]). For an enhanced understanding, the phase equilibrium investigations can be complemented with Tammann plots ([63], [66]-[71]), thermal cycling tests ([22], [27], [29], [34], [45]), and thermal annealing [38] or strain induced transformations [72]. In Tammann plots, eutectics or peritectics can be precisely identified by plotting their respective enthalpy change against composition. There, a eutectic or a peritectic takes a triangular shape, with the enthalpy maximum (peak) at the exact eutectic/peritectic composition [73]. The Tammann plot also indicates the systems' solid-state miscibility at the blend compositions where the eutectic or peritectic enthalpy becomes zero [73].

Hence, in this erythritol-xylitol experimental phase equilibrium investigation, several of these techniques and approaches: the T-history; TPS; Tammann plots; XRD; and FESEM were used in-combine for a comprehensive understanding. The purity of erythritol and xylitol used and their preparation are explained in section 2.1. To derive their phase diagram, primarily the phase change temperatures at various compositions are determined here using the T-history method. Through these measurements, the system's melting enthalpies and the specific heat (c_p) variations are also determined (section 2.2). To verify if the required conditions in the T-history are met, thermal conductivity of the pure components and some blends were determined using the TPS method (section 2.2). Then, to verify the obtained phase diagram, XRD-based crystallographic evaluations (section 2.4) and FESEM-based microstructural evaluations (section 2.5) were also performed on chosen compositions.

2.1 Materials

Meso-erythritol ($C_4H_{10}O_4$, CAS number 149-32-6) and xylitol ($C_5H_{12}O_5$, CAS number 87-99-0) of 99% purity each [74] were used in the study, with their details summarized in Table 1. The blend samples were prepared at the compositions: 2, 5, 10, 20, 25, 30, 35, 40, 50, 60, 70, 80, 90, 95, and 98 mol% Erythritol (termed mol% Er hereon) by weighing appropriate amounts of the pure components and by grinding them using a porcelain mortar and pestle. The overall mixing procedure here ensures a sample

composition with an expanded uncertainty of 1.3 mol%, within a 0.95 confidence⁴ (c.f. Appendix, section 7.1.3).

Table 1. Materials used in the study and their purity

Material	Source	Purity ^a	Further purification
Meso-erythritol	Alfa-Aesar [74]	99%	None
Xylitol	Alfa-Aesar [74]	99%	None

^aas specified by the supplier [74]

These samples were then kept under desiccation for 24 hours to remove any moisture absorbed during preparation. Succeeding desiccation, a simple thermo-gravimetric test (drying 10 g samples in an oven-Termarks TS4000- at 75 °C, while regularly measuring⁵ their weights until becoming constant, and also after 24 hours) was conducted on erythritol, xylitol, and, 25 and 80 mol% erythritol. This yielded weight losses smaller than 0.05%. Therefore, negligible moisture content was assumed in all the samples after 24 hours desiccation. The desiccated samples were then transferred into stainless steel (SS) test tubes (10 ml volume), for the T-history method: in powder form for temperature-tests; and in liquid form, after melting in an oven (Termarks TS4000) at 135 °C for 5 hours, for enthalpy-tests (further explained in section 2.2). The evaluated sample weights in the temperature-tests and enthalpy-tests respectively were between 10.02-11.35 g, and 14.02-15.90 g (with an expanded uncertainty of 0.04 g with a 0.95 confidence, with details in Table 7 and section 7.1.2 in the Appendix). The samples for the XRD and FESEM were prepared from the T-history end-products, further detailed in the sections 2.4 and 2.5.

2.2 Temperature-History (T-history) Method

In materials prone to supercooling, smaller samples tend to supercool more. Thus in this study the T-history method was chosen, which allows at least 1000-times larger samples and hence is advantageous over the DSC or IRT used in the previous erythritol-xylitol studies ([21], [33]). Thereby, it was expected to lessen the supercooling of this system containing components that exhibit supercooling as pure components (e.g. erythritol [29]). The T-history method employed here is explained elsewhere [22], [29], with slight modifications explained herein. The main criterion for the validity of the T-history evaluation is a small Biot number, i.e., below 0.1 [29], [75]. A small Biot number means that heat conduction dominates over convection, meeting the lumped capacitance conditions. In the enthalpy and specific heat (c_p) calculations in this work, the total heat gain of the reference block $\dot{Q}_R$ (in W) is expressed using a linear curve-fit with an intercept (Eq. 1), unlike in Gunasekara et al. [29]. The corresponding changes to the calculation are detailed here, while the overall concept remains the same. In Eq. 1, the slope k_1 is the product of the overall heat transfer coefficient U (W/(m²·K)) and the heat transfer area A (m²) as expressed in Eq. 2. The intercept k_2 is a constant (with the unit W).

$$\dot{Q}_R = k_1 \cdot \text{lmtd}_R + k_2 \quad \text{Eq. 1}$$

The overall heat transfer coefficient U (i.e., k_1/A) is the same for the reference and the PCM. This is because of the identical geometries of the PCM containment and reference, and these being maintained in the same conditions [75], [76]. The total heat gained by the PCM sample and its containment test tube (SSTT) ($\dot{Q}_{Tot}$) can be determined by solving Eq. 2 and Eq. 3. There lmtd is the logarithmic mean

⁴ Except for the 2 and 98 mol% Er used in the temperature-tests, which have an expanded compositional uncertainty of 5% and 4% Er (with 0.95 confidence) respectively, because there a weighing scale with an expanded uncertainty of 0.14 g with a 0.95 level of confidence was used.

⁵ Using a Mettler Toledo AX250 weighing scale with an expanded accuracy of 0.0003 g with 0.95 confidence.

temperature difference. As the mass m_{SSTT} (g) and the specific heat $c_{p,SSTT}$ (J/(kg·K)) of the SSTT and therefore the heat absorbed by it ($\dot{Q}_{SSTT}$) are known (c.f. [29]), the heat gained by the PCM ($\dot{Q}_{PCM}$) at each time step Δt (s) can be calculated using Eq. 4.

$$k_1 = U \cdot A = \frac{\dot{Q}_R - k_2}{lmt d_R} = \frac{\dot{Q}_{Tot} - k_2}{lmt d_{Tot}} = \frac{(\dot{Q}_{PCM} + \dot{Q}_{SSTT}) - k_2}{lmt d_{PCM}} \quad \text{Eq. 2}$$

$$\dot{Q}_{Tot} = \dot{Q}_{SSTT} + \dot{Q}_{PCM} = k_1 \cdot lmt d_{PCM} + k_2 \quad \text{Eq. 3}$$

$$\dot{Q}_{PCM} = k_1 \cdot lmt d_{PCM} + k_2 - \dot{Q}_{SSTT} = k_1 \cdot lmt d_{PCM} + k_2 - (m_{SSTT} \cdot c_{p,SSTT} \cdot dT_{SSTT} / \Delta t) \quad \text{Eq. 4}$$

Thereafter, the specific heat c_p and the overall thermal energy storage capacity of the PCM (material tested) over the chosen temperature range is calculated [29]. The T-history set-up was verified with benchmark tests conducted using distilled water and the alkanes: dodecane, tridecane and octadecane. The distilled water tests yielded identical temperature profiles, thus confirmed identical insulations. The measured enthalpies of the three alkanes (with an expanded uncertainty of 10% with 0.95 confidence, c.f. Appendix, section 7.1.4) were consistent with the literature data, and hence validate the T-history method.

Two separate T-history tests were conducted: temperature-tests and enthalpy-tests. The temperature-tests started with the powder samples in SS test tubes to also capture the very first melting behavior. However, after the first melting, the sample volumes decreased below the reference volume. Thus, the sample and reference geometries are not the same to assume the same thermal resistance. Therefore, the enthalpy-tests were then conducted using molten samples (pre-melted, c.f. section 2.1), with volumes the same as the reference. Thereby, the T-history conditions for a correct enthalpy calculation were achieved and the obtained enthalpies are given in section 3.1.2. However, starting with already molten samples, the enthalpy-tests exclude the first melting. Tammann plots were constructed (section 3.1.3) using the approximate enthalpies from the temperature-tests (calculated assuming the same sample and reference geometries, and that the error in doing so has the same effect on each enthalpy). This was done to also include the first melting in the Tammann plots.

Solid references made of electrolytic copper (Cu-ETP) and stainless steel (type SS 316) respectively were used, having the same geometry as the sample test tubes, and weighing respectively: 162.66 ± 0.04 g and 145.8 ± 0.04 g. Their thermal properties used are detailed in Table 2. The specific heat of SS 316 was used as a function of temperature based on the values in Table 2.

Table 2. Thermal properties of the reference and the test tube materials used in the T-history method (SS: stainless steel, ETP: electrolytic)

Material type	Specific Heat kJ/(kg·K)		Thermal Conductivity W/(m·K)	Remarks	Source
ETP copper (Cu-ETP)	0.39		389.1	Average between 20-100 °C	[77]
SS 316	0.452, 0.528 and 0.548	0.486,	*16.2	Respectively at 20, 90, 200 and 320 °C/ *At 100 °C	[78], [79]

The thermal sensors used were calibrated T-type thermocouples (of 0.4 °C expanded uncertainty with a 0.95 confidence level, c.f. Appendix, section 7.1.1). The sample test tubes and the references, once the

thermal sensors are inserted, were insulated with 19 mm thick HT-Armaflex. These were then kept inside a stainless steel containment box to prevent heat convection effects (c.f. Figure.A 1 in the Appendix). This whole set-up was then thermally cycled inside a temperature-programmable climate chamber at a heating and cooling rate of 0.2 °C/min, while maintaining isothermally for 5 hours at the highest and lowest cycle temperatures 0 °C and 139 °C. The fixed heating/cooling rates were used (instead of fixed temperature steps) to avoid metastabilities caused by the temperature asymmetry due to large supercooling of these polyols (e.g. erythritol [29]). In total, 8-9 or 5 complete heating and cooling cycles were conducted for temperature- and enthalpy-tests respectively (spanning over 7-10 days). In these T-history tests, 6-8 different compositions with one sample per each composition were evaluated simultaneously.

The compositions 0-60 mol% Er did not readily freeze after the very first melting, owing to their glassy nature. To induce crystallization (and melting at the subsequent heating) in these, 5-10 mg of the starting material was seeded into the supercooled liquid at around room temperature. Due to practical and time constraints, seeding was limited to only 3-4 cycles for these compositions. Thus the 0-60 mol% Er compositions melted only 4-5 times: the very first melting (only for temperature-test), and the succeeding 3-4 melting instances instated by the seeding-induced freezing. Since the cooling cycles were disturbed during seeding, these were excluded in the property calculations. Therefore, the results presented and synthesized here for the system are from the heating cycles only.

2.3 Transient Plane Source (TPS) Method

Since the blend thermal conductivities are unknown, as estimates, the thermal conductivity of erythritol, xylitol, and, 25 mol% and 80 mol% erythritol compositions were determined. For that, the Transient Plane Source (TPS) method using a Hot Disk Thermal Constants Analyzer TPS-2500S [80] was employed. There, the Hot Disk sensor 7577 of 2 mm radius, insulated with polytetrafluoroethylene (PTFE), and an in-house built aluminum sample holder (~7 ml capacity) mounted on an SS base were used [80]. Erythritol and xylitol were considered as the reference cases respectively for the 80 and 25 mol% blends.

2.4 X-Ray Diffraction (XRD)

XRD is the most used and straightforward technique to investigate crystallography. Hence, XRD was chosen here to evaluate the crystallography of the blend system to verify the phase change characteristics identified by the T-history. By comparing the XRD patterns of blends to those of the pure components, the details on the systems' miscibility and the types of the phases can be found. Using a Bruker D8 Discover XRD, three types of XRD investigations were conducted. The first was conducted at room temperature (referred to as RTXRD). The second was done using controlled heating from room temperature to a few degrees above the melting offset temperatures as identified with T-history (referred to as HTXRD). The third type included very slow heating and measurements at RT and at two chosen HT's (referred to as slow-XRD). The operating conditions used in the RT and HT tests are detailed in Table 3.

For the slow-XRD, the RT and HT conditions in Table 3 were used, plus 10 hours' isothermal steps and measurements for 10 hours at each chosen temperature. The samples preparation was similar for all the cases, where a solid block of each composition was grinded using mortar and pestle, and transferred to each sample holder. These samples were the end products of the T-history tests (after 5-9 cooling and heating cycles), then poured into glass test tubes at room temperature, and maintained at room temperature for 3 months (for RTXRD and HTXRD), or 1.5 months (for slow-XRD) respectively. The RTXRD

was conducted on the pure components and the compositions 5, 10, 20, 25, 30, 35, 40, 50, 60, 70, 80, 90, and 95 mol% Er. In the HTXRD it was expected to provide heating conditions (c.f. Table 3) rather close to that of the T-history, though not exactly the same. The compositions 5, 25, 30, 80 and 95 mol% Er were evaluated with the HTXRD. In the slow-XRD, the compositions 2 and 80 mol% Er were examined. There, to accommodate conditions more suitable for thermal equilibrium, isothermal steps at room temperature (for both 2 and 80 mol% Er) and at 70 °C and 76 °C (for 80 mol% Er) were employed.

Table 3. Operating conditions for the XRD tests conducted (XRD: X-ray Diffraction, RTXRD: Room-temperature XRD, HT-XRD: High- temperature XRD)

Operating Conditions	RTXRD	HTXRD
Sample holder	Polymeric material	Stainless steel holder with a Kapton Window
Radiation	Cu K α	
Detection type	1D Si strip detector, 192 strips	
Furnace	None	Antoon-Paar dome furnace DHS1100
Temperature calibration	None	Using pure erythritol and xylitol as references
Step size	0.03 degrees	0.03 degrees
Time per step (s)	1	0.3
Sample illumination	Fixed illumination of 10 mm	
Heating rate; Isothermal holding	None	1 °C/min; 5 min. (plus measurement time, ~3 min)
Selected temperatures (°C)	Room temperature	At ~5 °C intervals from room-temperature to ~5 °C above melting
2- θ range (scanning)	10-80	29-45

For both HTXRD (c.f. Table 3) and slow-XRD, the isothermal step temperatures were chosen based on the preliminary phase diagram (to include the possible single solid solution regions).

2.5 Field-Emission Scanning Electron Microscopy (FESEM)

The phase-indications found with the T-history and XRD measurements were expected to be further explained by microstructural evaluations on the system. Pre-tests from optical microscopy followed by a table-top SEM (TM1000) revealed a need for more powerful magnifications. An advanced SEM technique: Field-Emission SEM (FESEM), was thus employed, using the FESEMs Hitachi S-4800 and Jeol JSM-7800F. Most of the samples tested here by the FESEM were prepared using the T-history end-products (similar as in section 2.4). Many of these (5-95 mol% Er) were then annealed at room-temperature for 3 months (called long-term annealed samples). The 70 and 80 mol% Er compositions were also tested after quenching the T-history products to room temperature and annealing at this temperature for 1 day. These are called the short-term annealed samples. Expecting to retain the eutectic structure (if it exists) at the grain boundaries, several more samples were prepared. For that, molten T-history products of 5, 25, 32.5 and 80 mol% Er were annealed at 78 °C for 5 hours⁶, quenched in liquid N₂, and then annealed at room temperature for 3 hours. These are called the quench-annealed samples. For all FESEM investigations, flakes of the prepared solid samples were broken-off. These flakes were coated with Pt/Pd (the long-term and short-term annealed samples) or Au/Pt (the quench-annealed samples), using a sputter coater or a vacuum coater respectively. These coatings (5-8 nm of Pt/Pd or a 30 s cycle of coating with Au/Pt) were used to: avoid samples charging under the electron beam; improve the conductivity; and improve the topographical contrast of these materials with lower density [81].

⁶ Plus, annealing at 139 °C for 2 hours just for 80 mol% Er, to be able to pour the contents out, as it has solidified at 78 °C.

3 Results and Discussion

Here, the results of the comprehensive experimental phase equilibrium study on the erythritol-xylitol system are presented and discussed, with special focus on the new understanding of the system as compared to previous studies [21], [22], [33].

3.1 Thermal Property Characteristics from the T-history

The temperature, enthalpy, and c_p profiles of the T-history temperature-tests of certain erythritol-xylitol compositions (from the 17 investigated) for chosen melting cycles are summarized in Figure 1 (a)-(c). There, Er is erythritol, Xy is xylitol, M is melting, and the following number indicates the cycle number. The phase change onsets were deduced using a tangent each on the c_p peaks' leading edge and the baseline (see Figure.A 2 (c) in the Appendix), and for the offset vice-versa.

Figure 1. The (a) Temperature- (b) Enthalpy- and (c) Specific heat (c_p) profiles evolution of the erythritol-xylitol system, for the pure components and certain chosen blends at chosen melting cycles. (These profiles are shifted respectively by intervals of: (a) 60 min, (b) 70 kJ/kg, and (c) 10 (arbitrary units), for illustrative clarity. The c_p axis in (c) uses arbitrary units, however, with the gap between the minor gridlines similar to 4 kJ/(kg·K). M1-M4 indicate the 1st to 4th melting, while Er is erythritol, Xy is xylitol, and e.g. 2Er is 2 mol% erythritol)

As many c_p peaks lacked one straightforward leading edge, their phase change onsets and offsets were deduced by an overall comparison of the c_p , temperature, and enthalpy profiles. The phase diagram of the erythritol-xylitol system is constructed by plotting these deduced phase change temperatures versus the composition.

Figure 1 (c) shows that different compositions respectively had one, two, or three main phase change c_p peaks per heating. A single c_p peak indicated the melting of a single phase (e.g. erythritol, 95 and 98 mol% Er) or a potential eutectic (e.g. 25 and 30 mol% Er). If two or three c_p peaks appeared, the highest temperature peak was the melting, the one around the eutectic temperature was of the eutectic phase change, and a peak below the eutectic temperature was of a solid-solid phase change (S-SPC).

The compositions 20-60 mol% Er had a c_p peak with the onset at similar temperatures as in Figure 1 (c), implying a potential eutectic. An S-SPC occurred on the compositions 2, 5, 10, and 60 mol% Er during certain cycles, and on 70 and 80 mol% Er for all the seven cycles after the first melting, as e.g. in Figure 1. Often superheating accompanied the S-SPC, with a temperature increase before the plateau in the temperature profile and a negative c_p region before the melting c_p increment (e.g. 2, 70 and 80 mol% Er in Figure 1 (a) and (c)). Certain minor c_p peaks seen after the melting on some compositions (e.g. Figure 1 (c): Xy, Er, and 2 and 95 mol% Er) were excluded in the phase diagram, as these were subtle. These minor variations could be liquid-crystalline phase changes (like the mesophases in alkanes [82] and fats [83]), according to a guide on evaluating DSC c_p profiles [84]. However, these need to be verified. The c_p peaks of the S-SPC and the eutectic of certain compositions (e.g. 10 mol% Er, Figure 1 (c)) have a rather gradual increment that could indicate partially crystalline behavior [84]. Then the decreasing part of the melting peak reaches c_p values lower than that was for the solid phase, apparently implying decomposition [84]. This is confirmed by the browned and thicker final materials after thermal cycling, compared to the white crystalline (or transparent if molten) starting material, seen in all compositions. Phenomena like decomposition render the determination of an equilibrium phase diagram nearly impossible.

After the first melting of pure erythritol and xylitol certain minor phase change variations randomly appeared only during some melting instances (but not during others). These can be seen e.g. between 50-60 °C in Figure 1 (c) during the 3rd melting of xylitol and the 2nd melting of erythritol. Lopes Jesus et al. [42] reported a random appearance of a metastable S-SPC in erythritol at various temperatures (e.g. 15-43 °C or 65 °C respectively) in heating, before the stable melting. This metastable phase was a consequence of the previous cooling process, rather than the heating process [42]. Hence, the minor variations seen before melting in the present investigation could be such random metastable S-SPCs, or even consequences of evaluating large samples, or instrumental effects. Despite these minor deviations, pure erythritol and xylitol consistently displayed the stable melting peak corresponding to literature ([13], [21], [22], [28], [29], [39], [42], [52]-[58]), as seen in Figure 1. Hence, it could be considered that overall the T-history conditions reached stability.

The compositions 25 mol% Er (e.g. Figure 1) and 30 mol% Er had only a single phase change. This occurred around the eutectic temperature. Thus, 25 and 30 mol% are the closest to the eutectic point from those evaluated. Some compositions (e.g. 5, 70 and 80 mol% Er) had only a very subtle eutectic c_p change on certain cycles. For several compositions (e.g. 80, 90, 95 and 98 mol% Er), a eutectic c_p peak randomly appeared for some cycles but disappeared in some others. This could mean that the system in fact is partially miscible at these erythritol-rich compositions in the long-run. Similar observations were reported on e.g. the PG-NPG system where, for the compositions lower than 40-50% by weight only the

c_p peak corresponding to the high-concentration pure component was predominant⁷ [45]. That is, the PG-NPG system was predominantly partially miscible over long-term cycling (as XRD also verified) [45].

The system's phase diagrams of the real blends' melting, i.e. the 2nd-4th melting cycles, are compared with the temperature-composition plot of the first melting in Figure 2. During the very first melting of the mixtures, only the physically mixed powders of erythritol and xylitol melted and mixed in the liquid form for the first time (but not the melting of the real blend). Hence the temperature-composition plot for the first melting is included in Figure 2 merely for comparison. During the succeeding cycles, the freezing occurred from a single liquid (i.e., the real blend) followed by the melting of that frozen product, also involving seeding for 0-60 mol% Er compositions (similar to Siniti et al. [38]). In Figure 2, the average phase change of 2nd-4th melting cycles (called the selective average) is compared to: a) the temperature-composition plot of the first melting, and b) each 2nd-4th melting. Here, the expanded uncertainties of temperature and composition with 0.95 confidence (0.4 °C and 1.3 mol% Er) are indicated. The temperature uncertainty is so small that it is hidden under the data point markers.

Figure 2 represents two types of phase boundary choices, using either the phase change offsets only (right hand side column), or the eutectic and the S-SPCs onsets, and the melting offsets (left hand side column). There, the liquidus, solidus and the S-SPCs (i.e., solvus) are denoted with L, S and S-S respectively, followed by the cycle number. For the selective average no such number is used. The dotted lines in Figure 2 represent in a) the first melting, and in b) the phase boundary trends of the selective average using point-by-point interpolation (suffix 'int'). Generally, if only melting or a eutectic change appeared per heating, its onset and the offset were chosen as the solidus and the liquidus points respectively. When only a melting and an S-SPC occurred, the solidus and the liquidus points were the onset and the offset of the melting, and the S-SPC onset (or offset) was the possible solvus point. For a composition having both melting and a eutectic, these were included in one phase region: from the onset of the eutectic to offset of the melting, or offsets of both.

General trends in Figure 2 indicate a liquidus with a temperature minimum, and a rather isothermal spread of the solidus for many intermediate compositions for the 2nd-4th melting cycles. These altogether imply a possible eutectic isotherm with a eutectic in the system at around 30 mol% Er and a temperature around 77 °C (i.e., the eutectic onset). However, these features cannot be completely confirmed with the thermal properties (from T-history here) alone. A clear distinction between the phase change trends of the 1st compared to the 2nd-4th melting is seen in Figure 2 (a). Only the temperature-composition plot (yet not a phase diagram) for the first melting indicates the shape of a simple eutectic in a non-isomorphous system as proposed in literature ([21], [33]). The 2nd-4th melting cycles have a rather consistent phase change (except at 90-98 mol% Er, c.f. Figure 2 (b)), and contain S-SPCs e.g. on 2, 5, 10, 60, 70, and 80 mol% Er as shown in Figure 1. This behavior complies with Gunasekara et al. [22] but not with other studies [21], [33], and appears to indicate an incomplete solvus of a partially isomorphous system⁸. Hence, the system exhibits partial miscibility at pure component-rich compositions, as Gunasekara et al. [22] suggested. These S-SPCs make the solvus S-S (in Figure 2) while the incompleteness of this solvus may be due to glassy compositions. [85]

⁷ i.e., the pure component c_p peaks appeared till the 10th cycle, but afterwards (10th-100th cycle) only the c_p peak of the high-concentration component has occurred.

⁸ i.e., a system completely miscible in the liquid state but has partial miscibility in the solid state (i.e., contains a miscibility gap) [85].

Figure 2. Phase diagrams of the erythritol-xylitol system, comparing: the selective average (over 2nd-4th melting), with a) first melting, and b) each 2nd-4th cycles, respectively. (Left: for the onsets of eutectic and the S-SPCs and the melting offsets, Right: for offsets only).

A possible W shape of the liquidus around the probable eutectic (i.e., between 20-40 mol% Er) is observable at the 1st to 3rd melting cycles (marked in Figure 2 (a)). Gunasekara et al. [22] assumed a similar rise-and-fall in the liquidus as a possible congruent melting compound, which however needing crystallographic confirmations. This may be a co-crystal formation (a homogeneous crystal of two or more molecules bound by non-covalent bonds in fixed stoichiometry [86], i.e., a compound) similar to those reported on the xylitol-D-sorbitol and sorbitol-mannitol systems [47]. A co-crystal is a temperature maximum between two eutectics (in a W shaped liquidus) [86], forming a single sharp c_p peak and a new

XRD peak amongst the pure component peaks [47]. Overall, it appears that the erythritol-xylitol systems' phase equilibrium is complex and needs extensive experimental evidence to confirm the phase diagram.

The sensitivity of the phase change onset and offset temperature choices e.g. by evaluating the c_p curves as compared to the temperature measurement accuracy is depicted in Figure 3, using e.g. the 4th melting of 40 mol% Er. As in Figure 3, the eutectic onset temperature could be chosen to be 74.6 or 75.8 °C, based on the tangents' placement on the c_p peak. The difference between the two readings, 1.2 °C, is three times larger than the temperature accuracy (± 0.4 °C). For some transitions and many offsets however displayed sharper inflections and hence lesser deviations in the temperature choices. The liquid c_p in Figure 3 appears to be lower than that of the solid phase, indicating possible thermal decomposition (c.f. [84]).

Figure 3. The sensitivity of the phase change temperature choices on the c_p profile, identifying two possible inflection points. (The expanded uncertainty of temperature with 0.95 level of confidence is 0.4 °C)

Finally, comparing the use of onsets of eutectic and S-SPC and offsets of melting, or all offsets, to construct the phase diagram, the onset-offset combination is more preferred in this work (though different approaches were found employed, e.g. eutectic offsets as solidus [21] or melting peaks as liquidus [38]). In the phase diagram, the solid region below the eutectic isotherm should not contain any material that is still in the eutectic transition, so the eutectic onset is considered a better choice (Del Barrio et al. [33] used the same). Then the two-phase region is enclosed between the solidus and the liquidus by choosing the melting offset as the liquidus. The eutectic onset is a better choice as the solidus also because it is independent of the heating rate. The S-SPC was given less priority, so the choice could be either the onset or the offset. The other studies of the system [21], [33] chose the liquidus similarly. However, Diarce et al. [21] chose the eutectic offset for the solidus, to avoid complexities due to a partial-overlap of the melting and eutectic c_p peaks for some compositions. These methodology differences between the studies also account for their phase diagram discrepancies.

3.1.1 Thermal Conductivities

The thermal conductivities measured using the TPS method and the employed measurement conditions are summarized in Table 4. A smaller thermal conductivity results in a larger Biot number. As in Table 4, the blends' thermal conductivities were intermediate to that of xylitol and erythritol. Liquid erythritol has the smallest thermal conductivity, and therefore is the system's lowest possible thermal conductivity. It was thus used in the T-history calculations, and produced Biot numbers less than 0.1 for all the compositions. Thereby the lumped capacitance conditions and thus the validity of the T-history

evaluations are confirmed. To calculate the c_p and enthalpies, thermal conductivity is not an input (c.f. section 2.2), and thus their accuracy is unaffected by it.

Table 4. The thermal conductivities of pure erythritol, pure xylitol, and 25 and 80 mol% Er compositions^a

Sample	Liquid/ Solid	Temperature (°C)	Power (mW)	Time (s)	Thermal conductivity (W/m·K) ^d
Erythritol	Liquid	125 ^b	20	3	0.32
	Solid	20 ^c	20, 18-25	3, 2-4	0.59, 0.59 ^f
80 mol% Er ^e	Liquid	125 ^b	20	2	0.36
	Solid	20 ^c	20, 18-25	2, 2-3	0.55, 0.54 ^f
Xylitol	Liquid	110 ^b	20, 20-22	3, 2-3	0.41, 0.43 ^f
	Solid	20 ^c	20	3	0.37
25 mol% Er ^e	Liquid	110 ^b	20	2	0.40
	Solid	20 ^c	20, 22-25	3, 3-4	0.39, 0.39 ^f

^aThe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure (101±2 kPa)

^{b,c,d,e}the expanded uncertainty with 0.95 confidence level of: ^b5 °C; ^c0.1 °C; ^dup to 5%; and ^e1.3 mol%, respectively

^faverage over the range

3.1.2 Enthalpy characteristics

The enthalpies obtained from the T-history enthalpy-tests are summarized in Table 5. The phase changes were very subtle for 0-50 mol% Er after the first T-history melting, and for 25 and 30 mol% Er except for a subtle second melting. Hence, Table 5 represents the cycle with the most distinct phase change and/or the highest total phase change enthalpy per composition. In Table 5, the eutectic enthalpy (Δh_E) is the change between the onset and offset of the eutectic; the melting enthalpy (Δh_M) is the change between the offsets of the eutectic and the melting; the S-SPC enthalpy (Δh_{S-S}) is that between its onset and offset; and the intermediate sensible enthalpy change (Δh_{Intm}) is that between the S-SPC (or glass transition) offset and the eutectic onset (c.f. Figure.A 2 (b) in the Appendix). The total phase change enthalpy (Δh_{Tot}) is the sum of all the phase change enthalpies per composition, plus the Δh_{Intm} where relevant. ΔT_{Tot} is the temperature range of Δh_{Tot} .

In addition to melting, erythritol and xylitol also displayed a minor probable S-SPC (between 32.0-39.6 °C and 59.0-63.0 °C respectively), of which the enthalpies are shown in Table 5. The obtained melting enthalpies of pure erythritol and xylitol are 229±64 kJ/kg and 164±46 kJ/kg (c.f. Δh_M in Table 5), between 112.6-128.0 °C and 90.6-97.7 °C respectively. These values are lower than a majority of the enthalpies proposed in literature, but are closer (19-25% different) to the lowest literature values: 281-286 kJ/kg for erythritol [22], [29], [52], and 219-221 kJ/kg for xylitol [56] respectively. In fact, the stable melting enthalpies of erythritol and xylitol are proposed in literature with major discrepancies, between 281-370 kJ/kg ([13], [21], [22], [28], [29], [39], [42], [52], [53]-[55], [57], [58],) and 159-280 kJ/kg ([13], [21], [22], [29], [39], [40], [53]- [56]), within the temperatures 111-129 °C ([13], [21], [22], [28], [29], [39], [42], [52]- [55], [57], [58]) and 87-100 °C ([13], [21], [22], [29], [39], [40], [53]-[56]) respectively. These discrepancies could be related to the considerable dissimilarities among the studies on the employed apparatuses, heating rates, the temperature range of the presented enthalpy, and the number of cycles used.

As the enthalpy-tests here excluded the first melting (c.f. section 2.2), these obtained enthalpies are not exactly comparable with the many literature that represented only the first melting or an unspecified number of cycles ([13], [21], [28], [29], [39], [40], [42], [52]- [58]). Thermal degradation is known to lower polyols' enthalpies [27], [34], [41], and was found to occur only in air, but was avoided in anoxic conditions [27]. Hence, the ambient conditions in the T-history method potentially encourage thermal

degradation more than in inert conditions e.g. in a DSC [27]. Even with DSC, erythritol and xylitol melting enthalpies have decreased by 20% and 8%, after maintaining at 40 °C above the melting temperatures for 2 hours [34]. Therefore, thermal degradation most likely lowered the enthalpies of the samples assessed in this study (after the 5-9 T-history cycles). Moreover, glass transition and some random and minor metastable variations which may have occurred prior to the stable melting of erythritol and xylitol may also have reduced their melting enthalpies further.

Table 5. Phase change enthalpies of the studied erythritol-xylitol compositions, obtained using the T-history enthalpy-tests. (Here, Δh is the enthalpy change, with the subscripts indicating: S-S- solid-solid phase change; E- eutectic; M-melting; Tot-total; Intm- intermediate sensible enthalpy change; and other-other minor enthalpy changes due to e.g. possible glassy changes. The temperature range corresponding to Δh_{Tot} is ΔT_{Tot})

Composition mol% erythritol ^b	$\Delta h_{S-S}/\Delta h_{other}^c$	Δh_{Intm}^c	Δh_E^c	Δh_M^c	$(\Delta h_E + \Delta h_M)^c$	Δh_{Tot}^c	ΔT_{Tot}^d
	kJ/kg						°C
0	16	59	0	164	164	239	59.0-97.7
2	8 ^e	46	0	162	162	216	64.1-98.7
5	11 ^e	40	30	130.5	160.5	211.5	56.1-100.6
10	27 ^e	0	38	99	137	164	63.7-98.1
20	46 ^e	0	40	41	81	127	61.0-94.7
25	29 ^e	83	59.5	0	59.5	171.5	38.0-101.6
30	73 ^e	82	45	0	45	200	27.0-91.1
40	61 ^e	0	91	37	128	189	57.0-94.7
50	35 ^e	0	97	44.5	141.5	176.5	60.0-103.5
60	47	0	66	100.5	166.5	213.5	59.7-108.1
70	20	70.5	18.5	205	223.5	314	51.5-112.1
80	18	88	21	231	252	358	32.1-117.1
90	6	0	0	206	206	212	88.2-124.5
95	8	0	0	274	274	282	87.0-121.7
98	17	0	0	284	284	301	73.6-126.1
100	9.5	122.5	0	229	229	351.5	32.0-128.0

^aThe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure (101±2 kPa).

^{b,c,d}Expanded uncertainties with 0.95 confidence of composition, enthalpy and temperature are: ^b1.3 mol%, ^c28% and ^d0.4 °C.

^eA possibly glassy c_p change plateau/increase (but not a peak)

The maximum eutectic enthalpies of the compositions closest to the eutectic: 25 and 30 mol% Er are 59.5±17 kJ/kg and 45±13 kJ/kg (within 80.6-101.6 °C and 80.0-91.1 °C respectively), with the total enthalpy changes (including glass transition and the intermediate sensible enthalpy) around 172±48 kJ/kg and 200±56 kJ/kg. These are lower than pure components' melting enthalpies, however, being heavily influenced by glass transition, most likely are not their best enthalpies. The 40 and 50 mol% Er compositions exhibited the highest eutectic enthalpy, most likely because they were less influenced by glass transition while still have a considerable eutectic portion.

The enthalpy uncertainty for these polyols' T-history evaluation is rather high, i.e., 28% (expanded uncertainty with 0.95 confidence level). However, as an enthalpy estimate for a preliminary PCM assessment this is still valid. Here the enthalpy accuracy is proportionally influenced by the temperature accuracy (see Figure.A 3 in the Appendix). Thus, improving the temperature accuracy (by e.g. using more accurate thermal sensors like resistance temperature detectors-RTDs- instead of thermocouples) will produce a considerably accurate enthalpy.

3.1.3 Tamman plots

Figure 4 summarizes the Tamman plots of the erythritol-xylitol system. There, the molar enthalpy of the eutectic is plotted against the composition [73], using the enthalpies derived from the temperature-tests for 1st-4th melting. The plot for the 1st melting is shown for comparison, although it is not a correct plot because it does not represent the real blend melting. In Figure 4, the eutectic enthalpy change Δh_E (in kJ/mol) for each cycle is denoted with $h_{E,i}$ with a number identifying the cycle number. Simply h_E is the selective average over the 2nd-4th cycles. The uncertainty of these enthalpies derived from the T-history temperature-tests cannot be quantified, as they come with a volumetric error (c.f. section 2.2). This however, influenced each sample similarly.

Figure 4. Tamman plots of the eutectic in the erythritol-xylitol system, comparing the selective average of 2nd-4th melting (in a dashed line), with each melting cycle, 1st-4th (in dotted lines).

A Tamman plot characterizes a eutectic by a triangular shape with an enthalpy maximum at the exact eutectic (c.f. section 2). If the system is a non-isomorphous system forming a simple eutectic, the triangle ends at the pure compositions [73]. Whereas, if not, the triangle ends at the compositions where the eutectic diminishes and hence where the system is miscible in the solid-state. The erythritol-xylitol Tamman plots in Figure 4 lack a single triangle for any of the four cycles, and hence indicate a phase change behavior more complex than for a non-isomorphous system with a simple eutectic. Thus a linear regression analysis was also not possible on these plots. In addition, the eutectic enthalpy for several compositions varies considerably between the cycles. The real blend melting, i.e. at the 2nd-4th melting, indicates possible miscibility at pure component-rich compositions, where the eutectic enthalpy reaches zero. In contrast, the trend of the plot for the first melting (not the real blend) represents an immiscible system. The maximum eutectic enthalpy lies consistently at 25 mol% Er (for all the cycles), confirming that it is the composition closest to the eutectic. The liquidus trend of the selective average (Figure 2 (b)) indicates a temperature minimum around 30 mol% Er. Hence, it is reasonable to consider that the real eutectic may exist between 25 and 30 mol% Er (as compared to the others proposing it at 25 [21] or 36 [33] mol% Er).

3.2 Crystallographic Characteristics from XRD

In the RTXRD characteristics, all the major peaks of the blends corresponded only to a mixture of the peaks for pure erythritol and pure xylitol, and indicated no new or disappearing peaks (see Figure.A 4 (a))

in the Appendix). This implies that the two components are merely in a physical mixture in equilibrium at room temperature. The RTXRD alone indicates a non-isomorphous system at room-temperature, agreeing with Diarce et al. [21]. This system could be non-isomorphous with a simple eutectic, or forms a eutectic with partial miscibility at higher temperatures and undergoing de-mixing close to room temperature. However, the absence of peaks' disappearances for the blends in the RTXRD imply no solid solutions in the system, in contrast to the S-SPCs observed for some compositions (e.g. 2, 5, 10, 70 and 80 mol% Er) with the T-history. Therefore, HTXRD was conducted next, maintaining heating conditions rather close to the T-history conditions, expecting solid solution formation at higher temperatures. From the five compositions assessed with HTXRD, the XRD patterns of the 5 and 95 mol% Er are summarized in Figure 5, a) and b).

(a) 5 mol% Er, HTXRD heating from room temperature to above 94 °C

(b) 95 mol% Er, HTXRD heating from room temperature to above 124 °C

Figure 5. HTXRD characteristics of 5 and 95 mol% Er compositions, also identifying the erythritol and xylitol characteristic peak positions arrows marked with Er and Xy, respectively.

All the HTXRD compositions also displayed characteristic peaks for a physical mixture of the two pure components, but no new or disappearing peaks (i.e., no compounds or solid solutions in the system).

Therefore, the S-SPCs observed during the T-history cycles remain unexplained even with the HTXRD results. The reason for this discrepancy between the T-history and HTXRD was considered as due to the 5 times faster heating rate in HTXRD (1 °C/min compared to 0.2 °C/min used in the T-history method). Seemingly, the isothermal steps used during the HTXRD to create an apparent rate slower than 1 °C/min have also been inadequate to surpass the very slow kinetics of phase change in this glassy system. In addition, the counting statistics (e.g. the time per step) employed in HTXRD could have been insufficient to observe clearly the behavior of peaks. If so, the exact disappearance of some peaks of certain compositions (especially the extreme compositions 5 and 95 mol% Er) may be hidden. To clarify this, the measurement duration was significantly increased at each temperature as the next step, with slow-XRD.

From the slow-XRD assessments conducted (on 80 mol% and 2 mol% Er), the characteristics of 80 mol% Er are shown in Figure 6. As marked by arrows in Figure 6, the XRD peaks corresponding to xylitol in the 80 mol% Er sample, existing till 70 °C have disappeared at 76 °C. This indicates that, at and above 76 °C the blend has become a solid solution of erythritol (A solid solution S_A between two components A: the solvent and B: the solute, retains the crystal structure of the solvent A [87]). The 80 mol% sample below 76 °C then must be a mixture of a solid solution of erythritol and a solid solution of xylitol, as it shows the crystalline characteristics of both erythritol and xylitol in a mix. The slow-XRD of the 2 mol% Er (Figure.A 4 (b) in the Appendix) already at room temperature exhibited only the pure xylitol characteristics. This could be due to the very small volume fraction of erythritol in this blend.

Figure 6. Slow-XRD measurements summary on 80 mol% (xylitol peaks denoted by arrows), using 10 hours holding and 10 hours measurement at each temperature.

Finally, with the slow-XRD results, which represent the XRD conditions in this study closest to equilibrium, the partial miscibility of the erythritol-xylitol system is confirmed. This therefore corroborates the S-SPCs observed in the system, e.g. at 80 mol% Er. Hence, the system must have a solvus as the compositions 60-80 mol% Er indicate. With no new peaks observed even in slow-XRD, it can be concluded that the system does not form any new compounds or co-crystals, as was suspected with T-history only (section 3.1). The XRD results altogether confirm that the minor, probably metastable variations encountered in the pure polyols were not forwarded into the blend system. The XRD consistently displayed the characteristics of the stable solid erythritol and xylitol only, and hence implied the blends to have reached stability.

The detection limit in powder XRD is typically in the order of a few percent but depends on the instrument and sample. It can be seen from the RTXRD in the present work (Figure.A 4 (a) in the Appendix) that for the slow measurements the signal to noise ratio is quite high, and it is at least possible to identify erythritol peaks in the xylitol sample containing 5 mol% Er. The faster measurements however give a diffraction pattern with lower signal to noise and thus the detectable fraction is expected to be somewhat lower. From XRD it is further possible to identify solid solutions by interpreting the lattice parameters for the identified crystal structures, and will be further explored in future work.

3.3 Microstructural Characteristics from FESEM

Besides one hot-stage micrograph on the potential eutectic [21], no microstructural evaluations on the erythritol-xylitol system were found in open literature. Hence, this present work discloses the first FESEM investigations on the erythritol-xylitol system, to complement the phase change identifications from the T-history and XRD. From those evaluated (section 2.5), the selected compositions 5, 95, and 80 mol% Er are shown in Figure 7, detailing their microstructural indications on the systems' phase change. The magnifications are identified in the bottom of each micrograph, and the specific areas of interest are indicated in yellow. Here it is considered that the most stable crystal structure of erythritol is tetragonal [88], while that of xylitol is orthorhombic [43]. The interpretations are based on the findings so far which indicate that the system is partially miscible at the pure component-rich compositions (i.e., below around 10 mol% Er and, at and above 60 mol% Er), and contains a eutectic between 25-30 mol% Er.

Figure 7. FESEM images of a) 5 mol% Er, b) 95 mol% Er and c) 80 mol% Er specimens, which underwent: long-term annealing (a) 1), b) both, and c) 2)); short-term annealing (c) 1)); and quench-annealing (c) 2)).

The 5 mol% Er specimens exhibited a similar morphology for the long-term annealed and quench-annealed samples, as in Figure 7 a) 1)-3) (marked in yellow). There, one microconstituent⁹ (smaller blocks, e.g. Figure 7 a) 3)) of a minor proportion seem to have precipitated on the grain-boundaries of a matrix phase appearing as the continuous regions in specimens in Figure 7 a). The 10 mol% Er (not in Figure 7) and 95 mol% Er specimens (Figure 7 b) 1) and 2)) also exhibited similar grain-boundary precipitation of a microconstituent (as in Figure 7 b) 1)). These indicate a precipitation of a secondary

⁹ A microconstituent is a portion within a microstructure with a distinct structure [89]. An example is a eutectic microstructure.

microconstituent on a matrix (primary solid solution) phase, verifying the partial miscibility on the erythritol-xylitol system. The primary phase therefore is a solid solution of xylitol (S_{xy}) for 5 or 10 mol% Er, and a solid solution of erythritol (S_{Er}) for 95 mol% Er. The precipitated microconstituent is thus the eutectic portion of the hyper- or hypo-eutectic compositions. The rod-like shapes of the matrix phase hence are possibly orthorhombic for S_{xy} (in e.g. 5 and 10 mol% Er samples) and tetragonal for S_{Er} (in 95 mol% Er samples). The FESEM analysis further corroborates the partial miscibility of the erythritol-xylitol system in the solid-state. For instance, the 5, 10, and 95 mol% Er specimens seemingly contain a secondary precipitation of a microconstituent (i.e., the eutectic) on a primary solid solution (of the major constituent), when reaching stability at room temperature. [89]

The 70, 80 and 90 mol% Er samples formed cube-like crystalline blocks just as their T-history products (at $\sim 138^\circ\text{C}$) were quenched to room temperature. From these, e.g. the 80 mol% Er, investigated with FESEM after one day (i.e., short-term annealing) still contained these cube-like structures (c.f. Figure 7 c) 1)). Then, the microstructure of the same samples after long-term annealing was completely different. That (e.g. Figure 7 c) 2)), instead of cube-like crystals, had only a darker continuous microconstituent (circled region in yellow) surrounded by another lighter microconstituent precipitate. With solid solution formation confirmed at 80 mol% Er by both T-history and slow-XRD, this structure must represent the precipitation of the eutectic at a hypo- or hyper-eutectic composition on primary S_{Er} . As this structure (Figure 7 c), 2)) underwent the longest room temperature annealing, it has to be the most stable from those evaluated. Therefore, the cube-like structure in Figure 7 c) 1) is a metastable structure of the 80 mol% Er composition. Then again, the short-term annealed 80 mol% Er microstructure in Figure 7 c), 3) and 4) has a completely different morphology than those in Figure 7 c), 1) or 2) (compare the yellow indications). Hence, the structure as in Figure 7 c), 3) and 4) should also correspond to another metastable structure of 80 mol% Er. Overall, these metastabilities (of e.g. 70-90 mol% Er) indicate that the system's crystallization behavior is quite dependent on the rate and the process of cooling. This rate-specific behavior of the system is crucial to be known in TES design, regardless of the phases it contains.

3.4 The Discussion of the Binary Phase Diagram of the Erythritol-Xylitol System

From the three experimental methods employed to study the phase equilibrium of the erythritol-xylitol system, several complementary results are obtained, while some issues are still open for interpretation. The existence of a eutectic and the partial miscibility at the pure component-rich compositions are affirmed, whereas, determining the complete solvus needs more experimental/theoretical verifications. Nevertheless, using the obtained experimental evidences as a whole, the erythritol-xylitol phase diagram is proposed in Figure 8.

Figure 8 is constructed using the selective average phase change over the 2nd-4th melting cycles, with manually drawn phase boundaries to guide the eye, prioritizing the experimental points that denote a more fundamentally accurate trend. It excludes the first melting, as there only a physical mixture of the two pure component powders melted instead of a solid formed out of a single liquid. In Figure 8, the liquidus and the solidus represent the melting offset and the eutectic onset (c.f. section 3.1, and the phase diagram data in Table.A 3 in the Appendix). The solvus represents the S-SPC offsets, as they follow a more consistent increase towards the eutectic isotherm (compared to the onsets).

The current T-history results comply with the author's previous study [22]. However, lacking the physicochemical characteristics of the phase changes, there a more complex phase diagram was proposed [22]. The present study confirms the eutectic and the solid solutions, and rules-out the

possibility of compounds (or co-crystals) formation. Here, pure erythritol and xylitol experienced possibly metastable yet minor variations at certain cycles after the first melting, besides the consistent occurrence of the stable melting. These metastabilities perhaps lowered the melting enthalpy of the pure polyols. However, their phase diagram remained unaffected by them, as confirmed by the consistent display of only the stable solid characteristics of erythritol and xylitol, but no polymorphs, in the blends' XRD.

Figure 8. The erythritol-xylitol phase diagram proposal, a partially isomorphous system forming a eutectic. (The expanded uncertainty of temperature and composition are 0.4 °C and 1.3 mol% with 0.95 confidence respectively)

By combining the Tammann plots and the liquidus trends, the erythritol-xylitol eutectic in Figure 8 was chosen to be between 25 and 30 mol% Er compositions, and at the temperature 77 °C. In contrast, the others have proposed the eutectic around 25 mol% Er [21] or 36 mol% Er [33], and at 82 °C [21], [33]. Hence, the studies have considerable discrepancies between the proposed eutectic composition and temperature. The proposed phase diagram here: a partially isomorphous system with a eutectic, is also different to the non-isomorphous system with a simple eutectic proposed in literature ([21], [33]). Only the temperature-composition plot (not a phase diagram) of the first melting here indicated the shape of a simple eutectic in a non-isomorphous system. This major discrepancy is most likely related to the use of the cycled behavior excluding the first melting in this present work, compared to an unknown number of cycles used by other studies ([21], [33]).

Several more procedural differences may have contributed to the results mismatch between the studies. For instance, mixing a volatile solvent (diethyl-ether) to the blends to enable mixing [21] rather than using just the two polyols in blend (here). The solvent removal was not disclosed [21], which if not removed completely, could have influenced the phase change as an impurity. The sample size here was 1000 times larger (as opposed to a 'droplet' in the IRT method [33] or, 4-6 mg [21] or 10 mg [33] in the DSC), and most importantly the heating/cooling rates were 5 times slower than the 1 °C/min used by

others [21], [33]. Thus, the present study more likely represented the phase change behavior of bulk samples, and achieved conditions closer to equilibrium. Moreover, it is unclear if the overall thermal property evaluation methodology used here (section 3.1) matches those used by the others ([21], [33]) since those studies did not present details.

The melting enthalpy range of the eutectic lying between 25 and 30 mol% Er was found to be between 59.5 ± 17 kJ/kg and 45 ± 13 kJ/kg, with the total including that of glass transition between 172 ± 48 kJ/kg and 200 ± 56 kJ/kg. This was unfortunately heavily influenced by glass transition, and hence potentially the real enthalpy could be larger. This obtained eutectic enthalpy is not directly comparable with the eutectic enthalpies reported by the others: 249 kJ/kg [21] and 270 kJ/kg [33], as their phase diagrams are not comparable with Figure 8. Though the uncertainty of the obtained enthalpies is rather considerable (c.f. section 3.1.2), the phase diagram is unaffected by this. Only the temperature and compositional uncertainties influence the phase diagram, which are rather small (respectively, 0.4°C and 1.3 mol% expanded uncertainties within a 0.95 confidence level). The temperature uncertainty is negligible compared to the variations on the onset/offset temperature choice, as was explained in section 3.1.

As the glassy blends required seeding to realize freezing, the cooling cycles were excluded when constructing the phase diagram. However, the cooling-based phase diagram as well as the freezing enthalpies would have been valuable complements for TES design. Thereby the level of hysteresis and supercooling the blends including the eutectic undergo could be known, and the various phase changes observed in heating could be confirmed.

The erythritol-xylitol eutectic is attractive as a PCM e.g. for low-temperature solar heating, concerning its melting temperature, thermal conductivity, renewable origin and safety in handling. However, its main drawbacks are, the low melting enthalpy, and the extremely slow kinetics due to glass transition which prevents freezing or further melting after the first time on its own. A supercooling eutectic will phase separate, degrading its long-term storage capacity. Therefore, even for a TES that favors supercooling (to trigger freezing only when desired), this eutectic is unsuitable as a PCM. In addition, the blends, like their pure components, underwent thermally-activated change and thus risk losing the storage capacity in the long-term. Hence, the erythritol-xylitol eutectic should be further explored as a PCM to bypass glass transition to achieve phase change (e.g. by air bubbling [90], plasticizing with minute amounts of water [37], or stirring) and to further understand the thermally activated change. To confirm the exact eutectic of the erythritol-xylitol system, near-eutectic (i.e., within 25-30 mol% Er) compositions should be experimentally evaluated, combining T-history, XRD, FESEM, and Tammann plots. Likewise, to establish the solvus, compositions around the identified solvus points should be further evaluated experimentally. For this, interpreting the blend's lattice parameters using XRD to identify the solid solutions would be an effective complement. To confirm the standard behavior of the system, extensive cycling (e.g. 1000 cycles) of the blend system (similar to the PG-NPG study [45]) is recommended as future work. This can be coupled with phase-analysis to evaluate consistency in phase change with e.g. crystallographic and microstructural assessments.

In this study, the T-history method has been indispensable in the correct identification of the systems' equilibrium phase change, which e.g. consistently showed the solid-solid phase changes. The advantages of the method include the temperature, enthalpy, and c_p profiles that come together enabling a better phase change diagnosis, and the flexible operation allowing seeding. XRD has also been complementary to identify the eutectic. FESEM further confirmed the solid-solutions formation (and thus the partial

miscibility of the system in the solid-state) and implied metastable phase changes for some blend compositions at different cooling conditions. This exemplified the heating/cooling rate-dependent phase change of this system, important to be known in TES design. In the TES design scope, the methods T-history and XRD appear to be ideal candidates for phase diagram determination, and the FESEM an effective complement to refine the identified phase diagram.

To design PCMs from the erythritol-xylitol system, confirming its eutectic is essential, which requires the confirmation of the system's phase diagram. This necessitates the complementary use of several thermal and physicochemical property characterizations on the system, ensuring equilibrium conditions, and the standard behavior of the blend system in the long-run (e.g. under cycling). Even amidst disparities between the earlier studies ([21], [22], [33]) and the present study, the erythritol-xylitol phase diagram has evolved for the benefit of TES design. Each study has valuable scientific contributions, eventually building-up a database on this novel system with each upcoming finding. However, as this study shows, to collectively build-up knowledge on blend systems' phase equilibrium, the standardization of the property evaluation methodologies must continue for PCM design.

4 Conclusions

Through the current work, a thorough derivation of the phase diagram of the erythritol-xylitol system is presented. The T-history method, Tammann plots, XRD and FESEM were used in combination to derive this result. The key conclusions are summarized below.

- The system is partially isomorphous and contains a eutectic within 25-30 mol% Er at 77 °C, as compared to 25 or 36 mol% Er at 82 °C proposed by the other studies.
- The previous studies were not transparent in their procedural presentation, e.g. they appear to have excluded the cycling effect to conclude on the phase diagram.
- The system's temperature-composition plot of the first melting indicated the shape of a simple eutectic in a non-isomorphous system, while the phase diagram (of the subsequent melting cycles) exhibited partial miscibility.
- The eutectic in this system is attractive as a potential PCM if it has no supercooling (to avoid phase separation) and no thermally-activated change (to avoid decomposition), while glass transition and metastability (primarily cooling rate dependent behavior) are addressed.
- The partial miscibility of the system at solid-state is confirmed in this paper.
- The T-history method allowed seeding to capture the phase equilibrium behavior upon cycling, and the XRD corroborated these findings with slow heating and measurements (20 hours).
- The FESEM micrographs of the blends indicated the partial miscibility of the system in the solid-state, and the dependence of the systems' phase change on the cooling rate, tending to yield metastability at faster rates.

Constructing the complete phase equilibrium diagram of a novel blend system is an extensive process of continuous development. There, complementary phase diagram contributions expand the knowledge. For this, a common consensus in the PCM design context, on standard methodologies in deriving phase diagrams, is crucial. The theoretical phase equilibrium modelling of the system is being performed as the next step, to further verify the phase diagram of the system.

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7 Appendix

7.1 Uncertainty Calculations

The uncertainty calculations for temperature, mass, composition and enthalpy are briefly explained here. Their expanded uncertainty with a 0.95 confidence were then calculated by multiplying by the Z-score 1.96 (considering large populations).

7.1.1 Temperature Uncertainty

All the thermocouples were calibrated at a 10 °C temperature interval between -30 °C to 140 °C. To calculate their type A (due to scale linearity) uncertainty, the standard deviations from the calibration for each 10 °C step (from -30 °C to 140 °C) were averaged. This was found to be 0.18 °C. The type B (manufacturer-stated) uncertainty here is primarily due to the data logger, and was assumed as already counted via the thermocouple calibrations (conducted using the same logger). Thus the expanded uncertainty of temperature is found to be 0.4 °C (i.e., 0.18*1.96 °C) with a 0.95 confidence level.

7.1.2 Mass Uncertainty

For the T-history measurements, most of the erythritol-xylitol samples were weighed using an Ohaus Pioneer scale (scale 1), while the 2 and 98 mol% Er samples were weighed using a KERN FKB scale (scale 2). During the moisture measurements, the samples were weighted using a Mettler Toledo AX250 weighing scale (scale 3). Their type A and type B uncertainties, total uncertainty, and the expanded uncertainty with a 0.95 confidence level, are summarized in Table.A 1.

Table.A 1. Weighing scales' uncertainty calculations summary

Uncertainty type	Scale 1	Scale 2	Scale 3	Unit
Type A uncertainty	0.02	0.05	0.00010	g
Type B uncertainty	0.01	0.05	0.00010	g
Total uncertainty	0.02	0.07	0.00014	g
Expanded uncertainty with 0.95 confidence	0.04	0.14	0.00028	g

7.1.3 Compositional Uncertainty

The compositional (mol%) uncertainties depend on the mass measurement uncertainty for erythritol and xylitol. The corresponding uncertainty calculation was conducted using Eq. 5- Eq. 10. Here, σ is the uncertainty and m is mass, while the composition is expressed in terms of mol% Er. Er and Xy are erythritol and xylitol respectively. M is the molar mass, while k_3 (a constant), A' and B' are calculated according to Eq. 7 and Eq. 8 respectively.

$$\sigma(\text{mol}\%_{Er}) = \sqrt{\left(\frac{\partial(\text{mol}\%_{Er})}{\partial m_{Er}}\right)^2 \cdot \sigma m_{Er} + \left(\frac{\partial(\text{mol}\%_{Er})}{\partial m_{Xy}}\right)^2 \cdot \sigma m_{Xy}} \quad \text{Eq. 5}$$

$$\text{mol}\%_{Er} = \frac{\text{mol}_{Er}}{\text{mol}_{Er} + \text{mol}_{Xy}} \cdot 100 = \frac{m_{Er}/M_{Er}}{\frac{m_{Er}}{M_{Er}} + \frac{m_{Xy}}{M_{Xy}}} \cdot 100 \quad \text{Eq. 6}$$

$$k_3 = \frac{M_{Er}}{M_{Xy}} = \frac{122.12}{152.15} \quad \text{Eq. 7}$$

$$\frac{\partial(\text{mol}\%_{Er})}{\partial m_{Er}} = \frac{100k_3 \cdot m_{Xy}}{(m_{Er} + k_3 \cdot m_{Xy})^2} = A' \quad \frac{\partial(\text{mol}\%_{Er})}{\partial m_{Xy}} = \frac{-100k_3 m_{Er}}{(m_{Er} + k_3 \cdot m_{Xy})^2} = B' \quad \text{Eq. 8}$$

$$\sigma m_{Er} = \sigma m_{Xy} = \sigma m \quad \text{Eq. 9}$$

$$\sigma(\text{mol}\%_{Er}) = \sqrt{\sigma m \cdot (A'^2 + B'^2)} \quad \text{Eq. 10}$$

After calculating the mol% uncertainty for each evaluated composition, their average was obtained. By multiplying this average with 1.96, the expanded compositional uncertainties with 0.95 confidence were obtained for scale 1 ($\sigma m = 0.04$ g) and scale 2 ($\sigma m = 0.14$ g), to be 1.27 mol% and 4.77 mol% respectively.

7.1.4 Enthalpy Uncertainty

The enthalpy uncertainty in the T-history tests is considered to be influenced by the temperature and mass measurements of the PCM, and the corresponding calculation is explained using Eq. 11. The heat absorption/release by the reference was considered constant per each heating or cooling cycle, and therefore as not influencing the calculated enthalpy of the PCM. Here, σ is the uncertainty, of e.g. mass (m), temperature (T), or, temperature change (ΔT). SS is stainless steel, SSTT is the SS test tube, Amb is the ambience, n is any measurement instance, and k_1 and k_2 are constants.

$$dh_{PCM} = (k_1 \cdot \text{Imtd}_{PCM} + k_2) \frac{dt}{m_{PCM}} - \frac{m_{SSTT} \cdot c_{p,SS} \cdot \Delta T_{PCM}}{m_{PCM}} \quad \text{Eq. 11}$$

$$dh_{PCM} = \left(k_1 \cdot \left(\frac{\Delta T_1 - \Delta T_2}{\ln \frac{\Delta T_1}{\Delta T_2}} \right)_{PCM} + k_2 \right) \frac{dt}{m_{PCM}} - \frac{m_{SSTT} \cdot c_{p,SS} \cdot \Delta T_{PCM}}{m_{PCM}} \quad \text{Eq. 12}$$

$$\sigma_{dh,PCM} = \sqrt{\left\{ \left[\frac{\partial(\sigma_{dh,PCM})}{\partial(\Delta T_1)} \cdot \sigma(\Delta T_1) \right]^2 + \left[\frac{\partial(\sigma_{dh,PCM})}{\partial(\Delta T_2)} \cdot \sigma(\Delta T_2) \right]^2 + \left[\frac{\partial(\sigma_{dh,PCM})}{\partial(\Delta T_{PCM})} \cdot \sigma(\Delta T_{PCM}) \right]^2 + \left[\frac{\partial(\sigma_{dh,PCM})}{\partial m_{PCM}} \cdot \sigma m_{PCM} \right]^2 + \left[\frac{\partial(\sigma_{dh,PCM})}{\partial m_{SSTT}} \cdot \sigma m_{SSTT} \right]^2 \right\}} \quad \text{Eq. 13}$$

The uncertainty of a small enthalpy change $\sigma_{dh,PCM}$ is expressed in Eq. 13, and is simplified into Eq. 17. There, the partial derivatives of $\sigma_{dh,PCM}$ with respect to the parameters that influence its uncertainty, i.e. A-E, are determined using the expressions in Eq. 18 and Eq. 19. By calculating the average of $\sigma_{dh,PCM}$ over the phase change temperature range, the enthalpy uncertainty is determined. By multiplying this value by the Z-score 1.96, the expanded enthalpy uncertainty with a 0.95 confidence level was found

(10% for the alkanes: octadecane, dodecane and tridecane, and 28% for the polyols: erythritol, xylitol and their blends).

$$(\Delta T_1) = T_{PCM}^{n-1} - T_{Amb}^{n-1} \quad (\Delta T_2) = T_{PCM}^n - T_{Amb}^n \quad (\Delta T_{PCM}) = T_{PCM}^{n-1} - T_{PCM}^n \quad \text{Eq. 14}$$

$$\sigma(\Delta T_1) = \sigma(\Delta T_2) = \sigma(\Delta T_{PCM}) = \sigma(\Delta T) = 0.4 \text{ } ^\circ\text{C} \quad \text{Eq. 15}$$

$$\sigma m_{PCM} = \sigma m_{SSTT} = 0.04 \text{ g} \quad \text{Eq. 16}$$

$$\sigma_{dh,PCM} = \sqrt{[A \cdot \sigma(\Delta T_1)]^2 + [B \cdot \sigma(\Delta T_2)]^2 + [C \cdot \sigma(\Delta T_{PCM})]^2 + [D \cdot \sigma m_{PCM}]^2 + [E \cdot \sigma m_{SSTT}]^2} \quad \text{Eq. 17}$$

$$A = \left(\frac{k_1 \cdot dt}{m_{PCM}} \left(\frac{\ln \frac{\Delta T_1}{\Delta T_2} - \frac{1}{\Delta T_1}}{\left(\ln \frac{\Delta T_1}{\Delta T_2} \right)^2} \right) \right) \quad B = \left(\frac{k_1 \cdot dt}{m_{PCM}} \left(\frac{\frac{1}{\Delta T_2} - \ln \frac{\Delta T_1}{\Delta T_2}}{\left(\ln \frac{\Delta T_1}{\Delta T_2} \right)^2} \right) \right) \quad C = \frac{-m_{SSTT} \cdot c_{p,SS}}{m_{PCM}} \quad \text{Eq. 18}$$

$$D = \frac{-1}{m_{PCM}^2} \left[(k_1 \cdot l m t d_{PCM} + k_2) dt - m_{sstt} \cdot c_{p,SS} \cdot \Delta T_{PCM} \right] \quad E = \frac{-c_{p,SS} \Delta T_{PCM}}{m_{PCM}} \quad \text{Eq. 19}$$

7.2 Supplementary Data

The weights of the pure components employed to prepare each tested composition, and their sample weights that were measured in the T-history temperature-tests and enthalpy-tests (c.f. section 2.2) respectively are reported in Table.A 2.

Table.A 2. The compositions and weights of the samples tested with the T-history experiments^a. (SS: stainless steel)

Molar Composition ^b (%) erythritol)	0	2 ^g	5	10	20	25	30	35	40	50	60	70	80	90	95	98 ^h	100
Erythritol mass ^c (g)	0	0.29	1.22	2.47	5.04	6.36	7.71	9.09	10.50	13.42	14.37	10.30	17.14	18.02	17.85	13.30	35.00
Xylitol mass ^d (g)	35.00	16.59	28.91	27.66	25.10	23.77	22.42	21.04	19.63	16.72	11.93	5.50	5.34	2.49	1.17	0.33	0
Sample mass in SS test-tube ^e (g) (temperature-test)	11.35	10.58	10.46	10.58	10.61	10.02	10.72	10.53	10.62	11.46	11.32	11.35	10.69	10.46	10.87	10.35	10.05
Sample mass in SS test-tube ^f (g) (enthalpy-test)	15.9	15.72	14.86	14.16	14.79	14.88	14.59	None	14.14	14.08	14.52	14.19	15.42	15.84	14.32	14.02	14.56

^athe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure (101±2 kPa)

^bthe expanded uncertainty, of the molar composition, with a 0.95 level of confidence is 1.3%

^{c,d,e,f}the expanded uncertainty, of mass, with a 0.95 level of confidence is 0.04 g

^{g,h}For the 2 and 98 mol% Er compositions, in the temperature-test, as a different weighing scale had to be used, with the expanded uncertainty with a 0.95 level of confidence: of mass 0.14 g; and of the compositions 2 and 98% Er being ±5% and ±4% Er.

The T-history set up (c.f. section 2.2) is further explained in Figure.A 1 using a photograph and a schematic.

Figure.A 1. The T-history set-up (Left: a photograph, Right: a schematic)

The phase change temperatures deduction (in section 3.1) is exemplified here further using the thermal properties of a chosen blend composition in the erythritol-xylitol system: the 10 mol% Erythritol (referred to as mol% Er hereon), for the 3rd melting, in Figure.A 2. As seen in Figure.A 2 (c), the 3rd melting of the 10 mol% Er exhibits three distinct c_p peaks for a solid-solid phase change (S-SPC), a eutectic phase change and melting respectively. These are, however, less pronounced in the enthalpy and temperature profiles (Figure.A 2 (a) and (b)). Nonetheless, the temperatures identified in the c_p curve were used to deduce the corresponding enthalpy changes (Δh), as in Figure.A 2 (b), for the melting, eutectic and S-SPC (denoted with the subscripts M, E, S-S), and for the intermediate sensible enthalpy change between the E and the S-SPC: Δh_{intm} .

Figure.A 2. The thermal properties of the third melting of 10 mol% Er, which contains an S-SPC, eutectic and melting. Here, T : temperature (°C), t : time (s), Δh : enthalpy change (kJ/kg), c_p : specific heat (kJ/(kg·K)).

The sensitivity analysis for the relation between the temperature and enthalpy uncertainty in T-history method is shown in Figure.A 3 (in relation to section 3.4). The expanded uncertainty of the temperature and enthalpy of the T-history set-up used here were 0.4 °C and 28% (kJ/kg) respectively, with a 0.95 confidence.

Figure.A 3. The sensitivity of the enthalpy uncertainty over the temperature uncertainty

In Figure.A 4, the RTXRD characteristics of erythritol, xylitol, and their blends (in (a)), and the slow-XRD characteristics observed on the 2 mol% Er (in (b)), are shown, as supplements to the details in section 3.2.

Figure.A 4. The (a) RTXRD pattern of pure erythritol, pure xylitol, and their blends, and (b) Slow-XRD of 2 mol% Er.

The phase diagram data of the erythritol-xylitol binary phase diagram presented in section 3.4 are detailed in Table.A 3, along the temperatures and the phases present, concerning the selective melting of the 2nd-4th cycles (as found in the T-history thermal cycling).

Table.A 3. Phase diagram data of the final proposed erythritol-xylitol phase diagram^a (for the selective average of 2nd-4th melting cycles). Here, Er and Xy are the pure solids of erythritol and xylitol, while S_{Xy} and S_{Er} are their solid solutions. L is the liquid, and t is the temperature in °C, with the subscripts s-s, S and Liq representing respectively the solvus, the solidus and the liquidus.

mole fraction, x_{Er}^b	Temperatures ^c and the phases present							
	ts-s, (°C)		Phases	tS, (°C)		Phases	tLiq,offset (°C)	Phases
	onset	offset		onset	offset			
0	na	na	na	na	na	na	95.2	Xy
0.02	55.2	57.7	S _{Xy} + S _{Er}	88.6	88.6	S _{Xy} + L	95.6	S _{Xy} +L
0.05	49.9	58.1	S _{Xy} + S _{Er}	79.3	82.9	S _{Xy} + L	92.6	S _{Xy} +L
0.1	52.0	63.7	S _{Xy} + S _{Er}	75.9	83.1	S _{Xy} + L	92.1	S _{Xy} +L
0.2	na	na	na	77.4	83.1	S _{Xy} + S _{Er} + L	87.1	S _{Xy} +L
0.25	na	na	na	76.7	86.7	S _{Xy} + S _{Er} + L	87.8	S _{Xy} +L
0.3	na	na	na	76.7	84.1	S _{Xy} + S _{Er} + L	85.1	S _{Er} + L
0.35	na	na	na	77.1	83.5	S _{Xy} + S _{Er} + L	86.2	S _{Er} + L
0.4	na	na	na	76.5	84.0	S _{Xy} + S _{Er} + L	91.4	S _{Er} + L
0.5	na	na	na	78.6	85.5	S _{Xy} + S _{Er} + L	101.7	S _{Er} + L
0.6	59.9	74.3	S _{Er} + S _{Xy}	78.1	83.6	S _{Xy} + S _{Er} + L	103.9	S _{Er} + L
0.7	48.6	50.4	S _{Er} + S _{Xy}	80.3	82.8	S _{Er} + L	110.1	S _{Er} + L
0.8	26.0	31.4	S _{Er} + S _{Xy}	71.9	77.3	S _{Er} + L	113.9	S _{Er} + L
0.9	na	na	na	91.4	93.6	S _{Er} + L	117.1	S _{Er} + L
0.95	na	na	na	102.2	102.8	S _{Er} + L	119.6	S _{Er} + L
0.98	na	na	na	97.7	98.0	S _{Er} + L	119.7	S _{Er} + L
1	na	na	na	na	na	na	120.7	Er

^aThe experimental pressure was not controlled in the study, beyond the typical atmospheric pressure 101±2 kPa

^{b,c}The expanded uncertainties of the molar composition and temperature are 1.3% and 0.4 °C respectively, with a 0.95 level of confidence