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Supplementary Information

Kinetics of Water-Induced Amorphous Phase Separation in Amorphous Solid Dispersions via Raman Mapping

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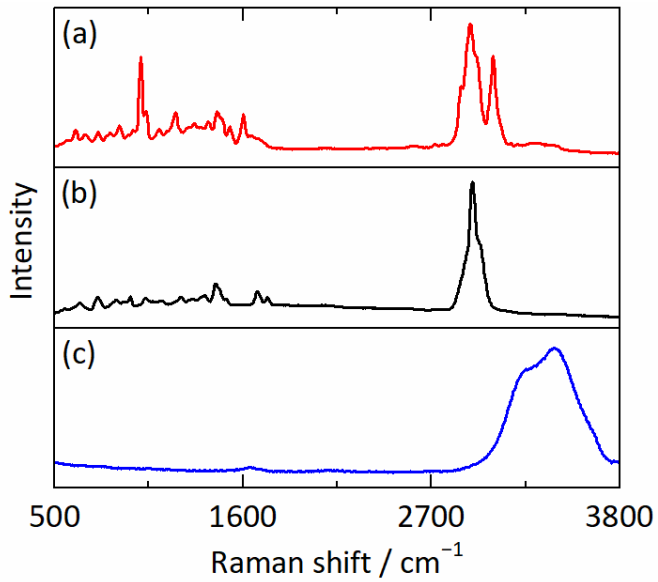

Figure S1. Pure component spectra of (**a**) amorphous RIT, (**b**) PVPVA, and (**c**) water at 25 °C.

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Table S1. Compositions of samples for calibration spectra at 25 °C

	w_{RIT}	w_{PVPVA}	w_{water}
Pure components	1	0	0
	0	1	0
	0	0	1
RIT/PVPVA	0.1	0.9	0
	0.2	0.8	0
	0.7	0.3	0
PVPVA/water	0	0.05	0.95
	0	0.10	0.90
	0	0.69*	0.31*
	0	0.85†	0.15†

* According to a gravimetric water sorption measurement after storage at 94% RH [11].
† According to a gravimetric water sorption measurement after storage at 74% RH in this work.

S1. Statistical Indicators

The statistical indicators R_i^2 (coefficient of determination), $RMSEC_i$ (Root Mean Square Error of Calibration), $RMSECV_i$ (Root Mean Square Error of Cross-Validation), $BiasC_i$ (Mean of the differences of calibration) and $BiasCV_i$ (Mean of the differences of Cross-Validation) were calculated for every component by using Equations S1-S5.

$$R_i^2 = 1 - \sum_k^{NP_i} \frac{w_{i,k}^{\mathrm{meas}} - w_{i,k}^{\mathrm{true}}}{w_{i,k}^{\mathrm{true}} - \overline{w}_i^{\mathrm{true}}} \tag{S1}$$

$$RMSEC_i = \sqrt{\frac{1}{NP_i} \sum_k^{NP_i} \left(w_{i,k}^{\mathrm{meas}} - w_{i,k}^{\mathrm{true}}\right)^2} \tag{S2}$$

$$RMSECV_i = \sqrt{\frac{1}{NP_i} \sum_k^{NP_i} \left(w_{i,k}^{\mathrm{meas,CV}} - w_{i,k}^{\mathrm{true}}\right)^2} \tag{S3}$$

$$BiasC_i = \frac{1}{NP_i} \sum_k^{NP_i} w_{i,k}^{\mathrm{meas}} - w_{i,k}^{\mathrm{true}} \tag{S4}$$

$$BiasCV_i = \frac{1}{NP_i} \sum_k^{NP_i} w_{i,k}^{\mathrm{meas,CV}} - w_{i,k}^{\mathrm{true}} \tag{S5}$$

$w_{i,k}^{\mathrm{meas}}$ is the measured mass fraction, $w_{i,k}^{\mathrm{meas,CV}}$ is the cross-validated measured mass fraction and $w_{i,k}^{\mathrm{true}}$ is the true mass fraction at data point k of in total NP_i data points of component i. $\overline{w}_i^{\mathrm{true}}$ is the mean true mass fraction of in total NP_i data points of component i. The statistical indicators for the calibration results are reported in Table S2.

Table S2. Calibration results in statistical indicators

	RIT	**PVPVA**	**water**
R_i^2	0.9994	0.9992	0.9996
$RMSEC_i$	0.0082	0.0112	0.0080
$RMSECV_i$	0.0118	0.0180	0.0137
$BiasC_i$	−0.0026	0.0064	−0.0038
$BiasCV_i$	−0.0010	0.0023	−0.0013

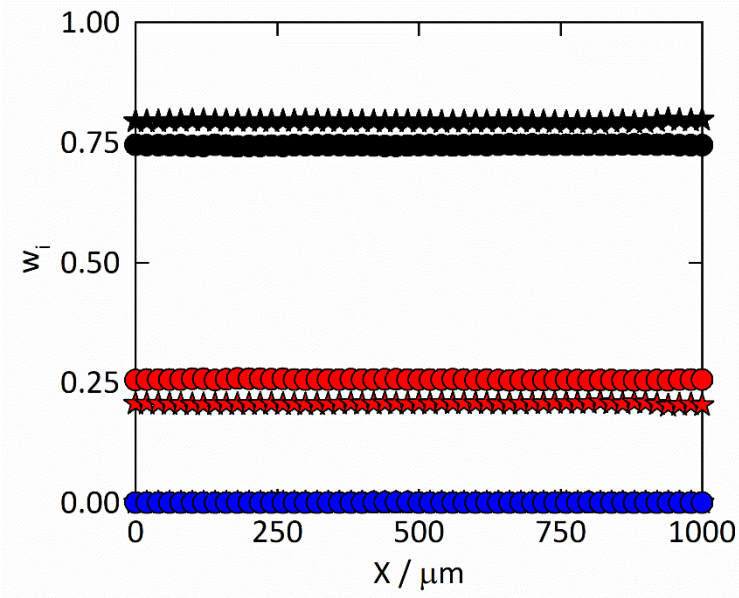

Figure S2. Mass fractions of RIT (red), PVPVA (black) and water (blue) in a freshly-prepared 20 wt% (stars) and 25 wt% (circles) DL RIT/PVPVA ASD obtained from 1000 µm line scans at 25 °C.

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