Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.
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Table S1 Characteristic temperatures (°C) of glass frit for P free $CaCl_2$ containing glasses.

Glass Code	T_g	T_{o1}	T_{c1}	$T_{c2/c3}$	T_{m1}	$T_{m2/m3}$	T_{o1}-T_g
GCl 0.0	782	922	958	1020	-	-	140
GCl 2.2	768	919	948	-	-	-	151
GCl 3.3	757	906	927	-	-	-	149
GCl 4.3	749	892	913	-	-	-	143
GCl 6.6	728	875	901	-	-	-	147
GCl 9.3	697	850	880	-	-	-	153
GCl 11.9	673	837	867	-	-	-	164
GCl 16.1	639	803	842	-	1061	-	164
GCl 27.4	528	700	736	-	806	891/1062	172
GCl 33.5	491	637	669	-	822	890/1062	146
GCl 43.0	429	528	560	-	778	892/1060	99
GCl 53.1	370	432	450	607/650	782	898/1060	62

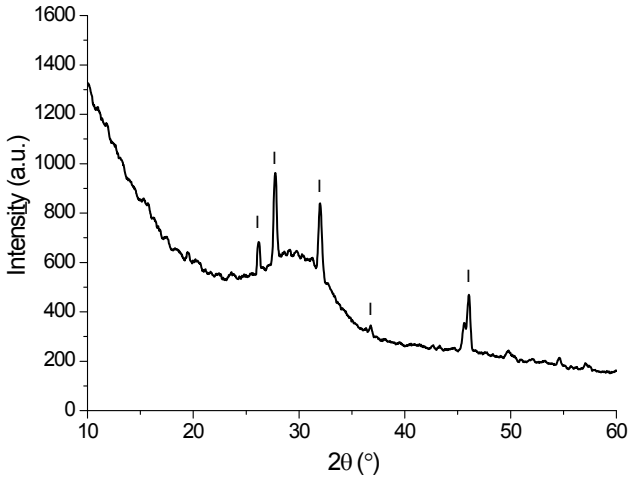

Fig. S1 The XRD pattern of the as-quenched glass GCl 0.0 presenting peaks at 25.99°, 27.56°, 31.7°and 45.91° 2θ (I: β-CaSiO3).

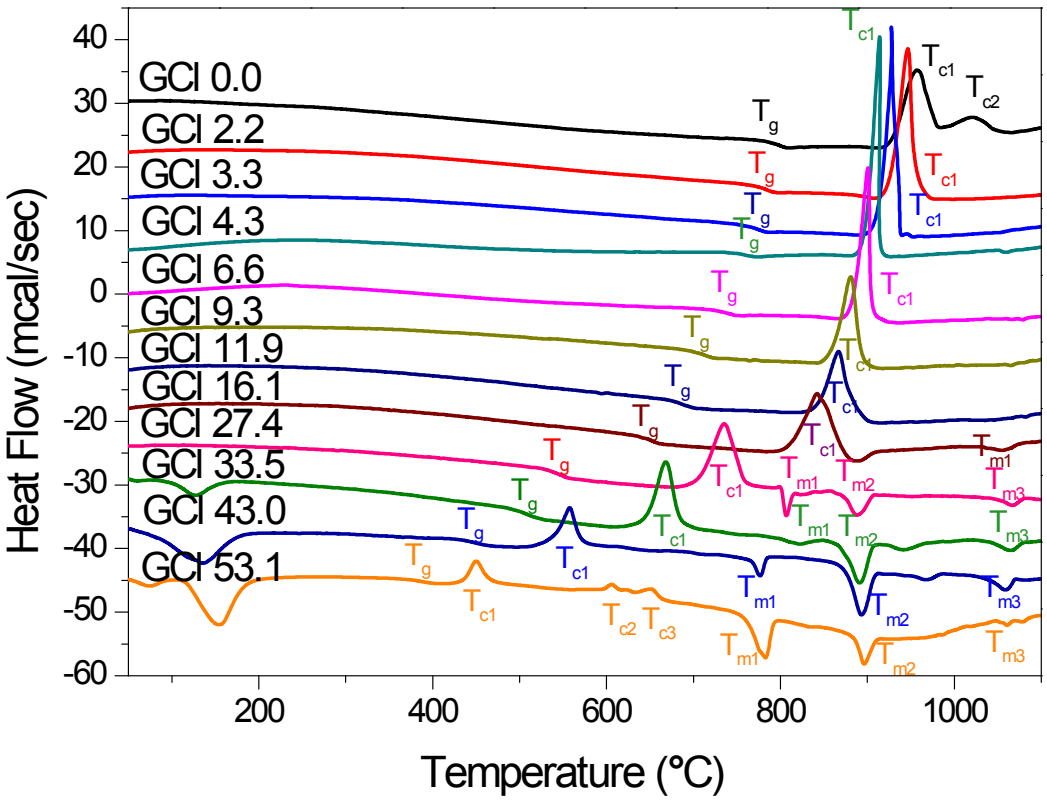

Fig. S2 DSC traces for the glass frits of $CaCl_2$ containing glasses with annotations with the characteristic temperatures.

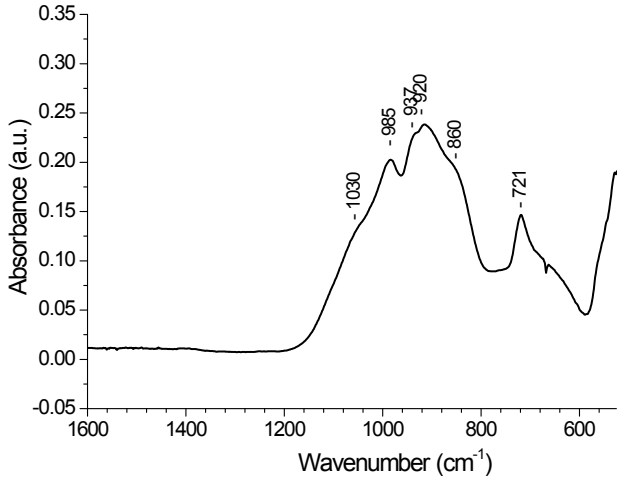

Fig. S3 The FTIR spectrum of glass GCl 0.0 (0.0 mol% $CaCl_2$).

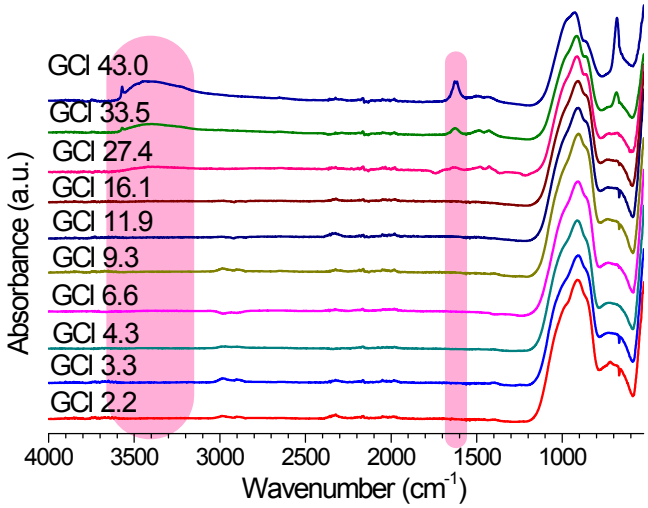

Fig. S4 The FTIR spectra of as-quenched glasses.

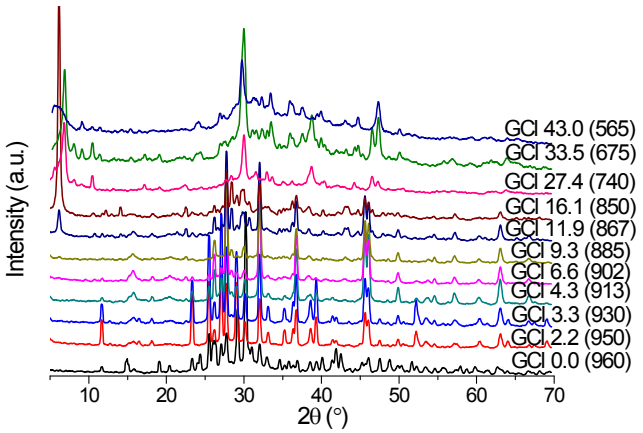

Fig. S5 Overview for the XRD patterns of the GCl glass series upon heat treatment. The numbers in the brackets represent the heat treatment temperature (°C).

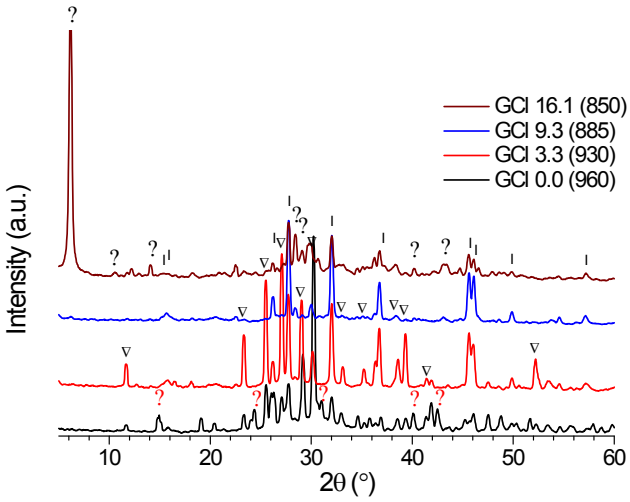

Fig. S6 The XRD patterns of the GCl glass series ($CaCl_2$ content ≤ 10.5 mol%) upon heat treatment. The numbers in the brackets represent the heat treatment temperature. (^{I}: β-CaSiO3; $^{\nabla}$: CaSiO3; $^{?}$: UP (unidentified phase) I; $^{?}$: UP II)

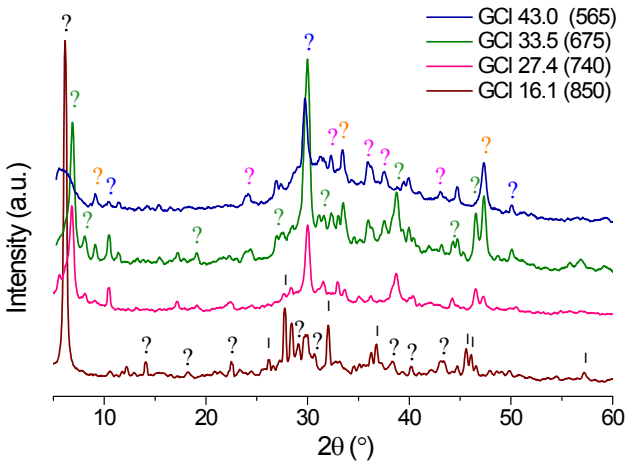

Fig. S7 The XRD patterns of the GCl glass series ($CaCl_2$ content ≥ 8.2 mol%) upon heat treatment. The numbers in the brackets represent the heat treatment temperature. (^{I}: β-CaSiO3; $^{\nabla}$: CaSiO3; $^{?}$: UP II; $^{?}$: UP III; $^{?}$: UP IV; $^{?}$: UP V)

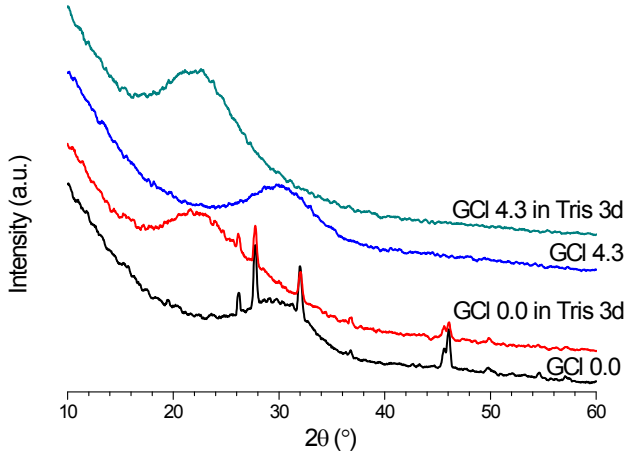

Fig. S8 The XRD patterns of the glass precipitates with 0 and 3.1 mol% $CaCl_2$ collected after 3 days immersion in Tris.