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Supporting Information

Ag^{+} heavily doped and single pulse nJ laser writable glass with ionic $[YO_6]$ modified covalent $Al(PO_3)_3$ networks towards long-term 3D optical data storage

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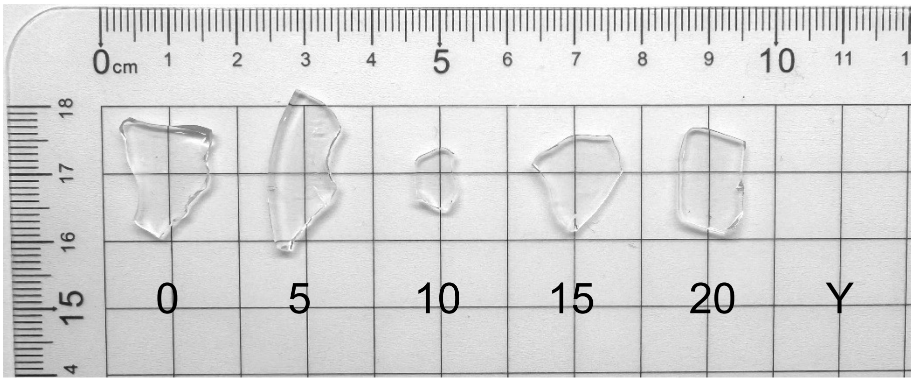

Figure. S1. Schematic diagram of (95-x)$Al(PO_3)_3$-x$YO_{1.5}$-5Ag_2O (x=0,5,10,15 and 20) glasses.

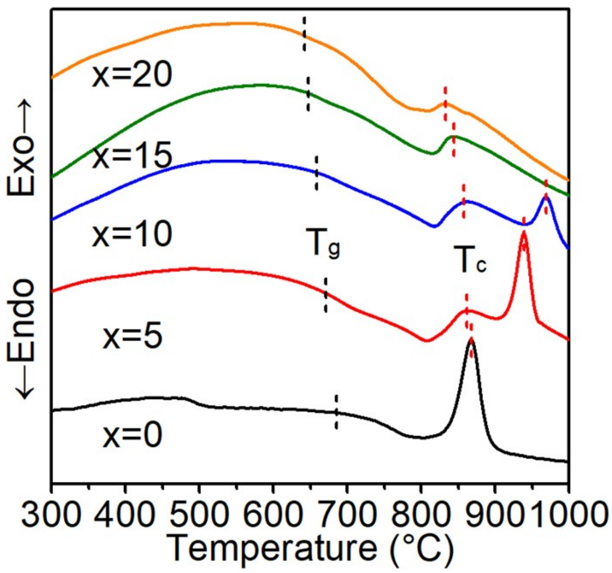

Figure. S2.DTA curve of (95-x)$Al(PO_3)_3$-$xYO_{1.5}$-$5Ag_2O$ (x=0,5, 10 ,15 and 20) glasses.

Supplementary Table 1. DSC curves assignments

Sample	T_g (°C)	T_{c1} (°C)	T_{c2} (°C)	$\triangle T=T_{c1}-T_g$ (°C)
x=0	685.6	867.0		181.3
x=5	670.3	861.5	937.2	191.2
x=10	658.0	857.5	968.4	199.5
x=15	646.8	842.0		192.5
x=20	642.0	831.3		189.4

Supplementary Table 2. Test results of mechanical properties of glass samples.[1]

	Sample	Elastic modulus (GPa)	Max compressive stress (MPa)
G1	$95Al(PO_3)_3$-$5Ag_2O$	28.46	142.33
G3	$85Al(PO_3)_3$-$10YO_{1.5}$-$5Ag_2O$	32.92	164.58
G5	$75Al(PO_3)_3$-$20YO_{1.5}$-$5Ag_2O$	37.23	186.15

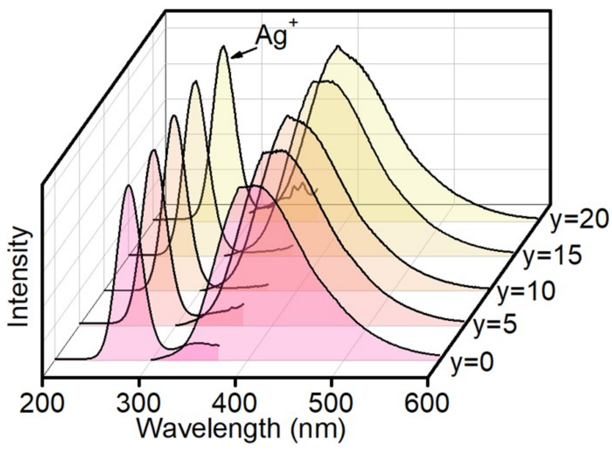

Figure S3. Photoluminescence spectra of (95-x)$Al(PO_3)_3$-$xYO_{1.5}$-$5Ag_2O$ (x=0, 5, 10, 15 and 20) glasses.

Table S3. Corresponding bond length of G1 and G5 glasses by AIMD.

G1	Distance (Å)	G5	Distance (Å)
Al-O	1.88	Al-O	1.86
P-O	1.59	P-O	1.56
Ag-O	2.60	Ag-O	2.38
Ag-Ag	9.17	Ag-Ag	9.34
		Y-O	2.42

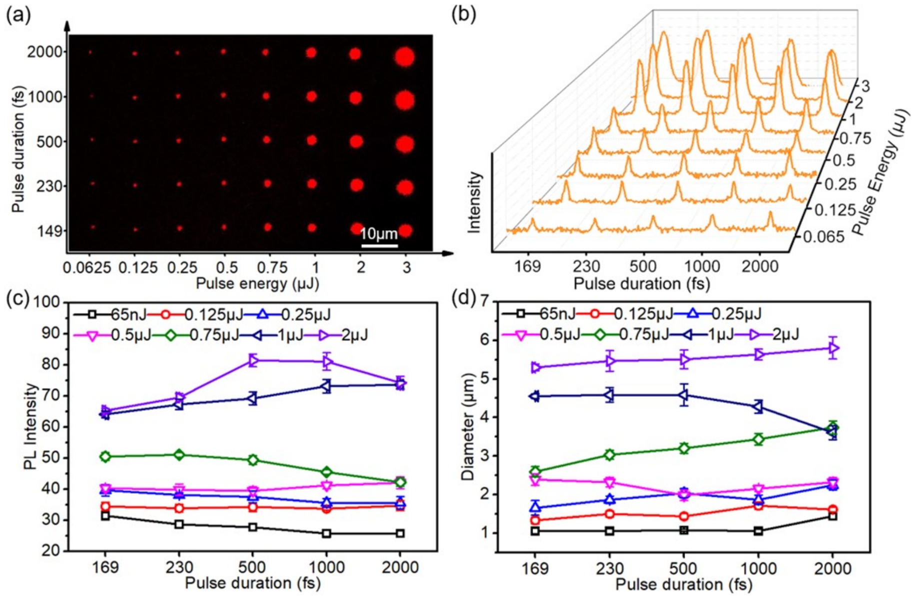

Figure S4. (a) Confocal fluorescence image of G5 glass, λ_{ex}=405nm. (b) Integrated PL intensity. (c-d) Dependence of PL intensity and domain diameter on laser energy and pulse duration.

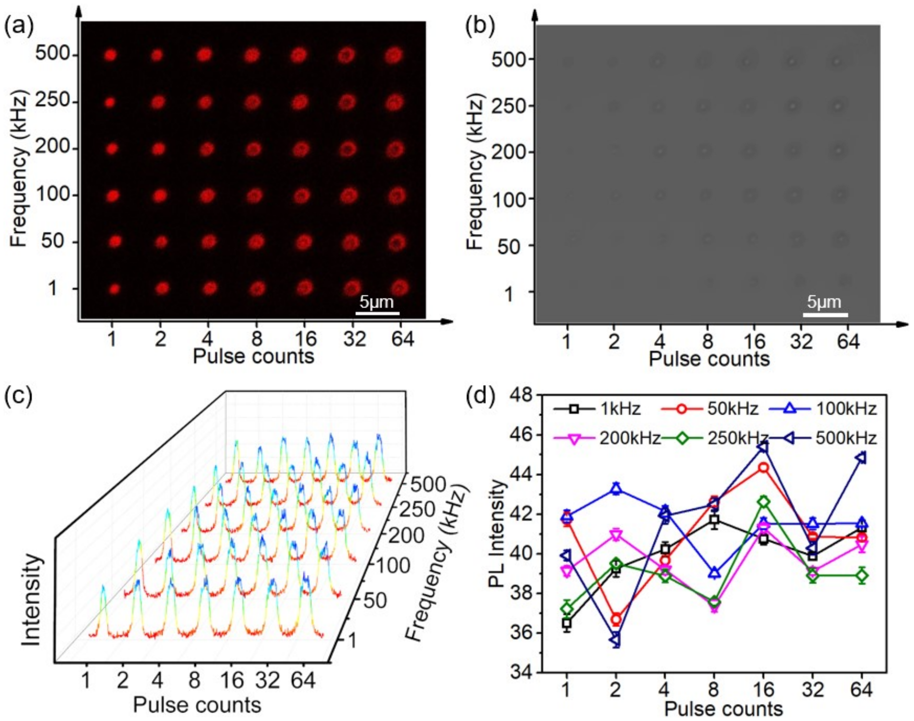

Figure S5. (a) Confocal fluorescence image of G5 glass, λ_{ex}=405nm. (b) Optical image of G5 glass. (c) Integrated PL intensity. (d) Dependence of PL intensity on pulse counts and frequency.

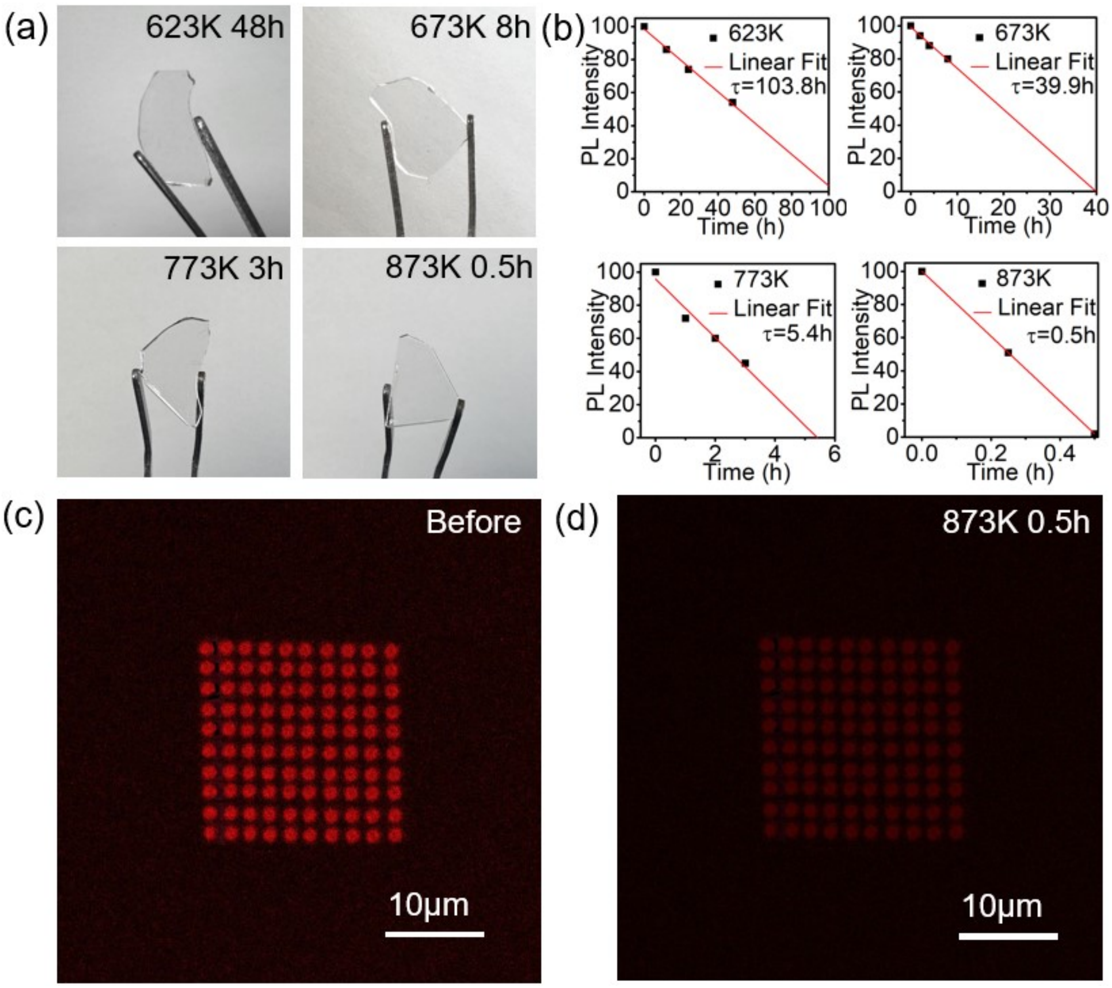

Figure S6. (a) Schematic of G5 glass after laser processing and heat treatment at 623 K for 48 h, 873 K for 8 h, 773 K for 3 h, and 873 K for 0.5 h (background: A4 paper). (b) Lifetime fitting curves after heat treatment at different temperatures. Confocal fluorescence mapping images of the laser-writing region: (c) before heat treatment and (d) after 873 K for 0.5 h heat treatment.

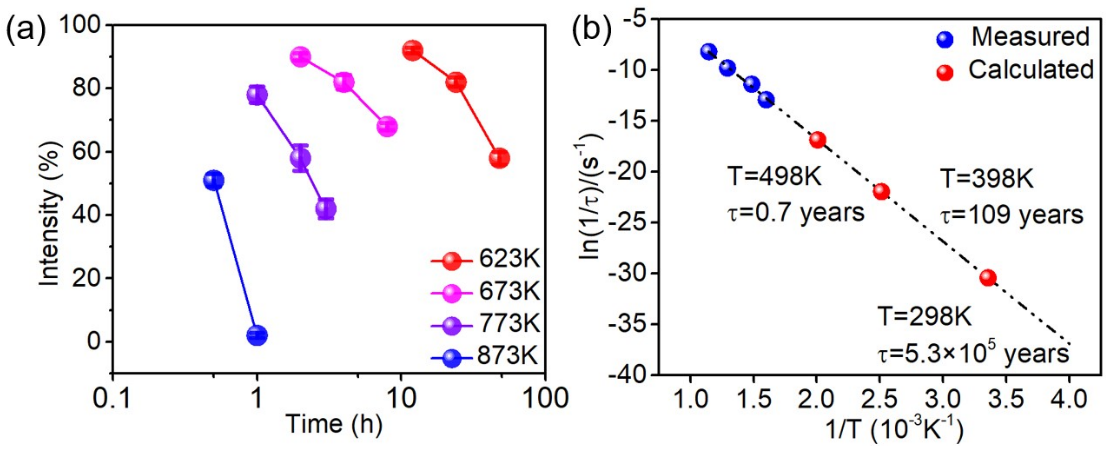

Figure S7 (a) Thermal stability of written pattern at pulse energy of 19 nJ and (b)

Arrhenius plot of the decay rate.

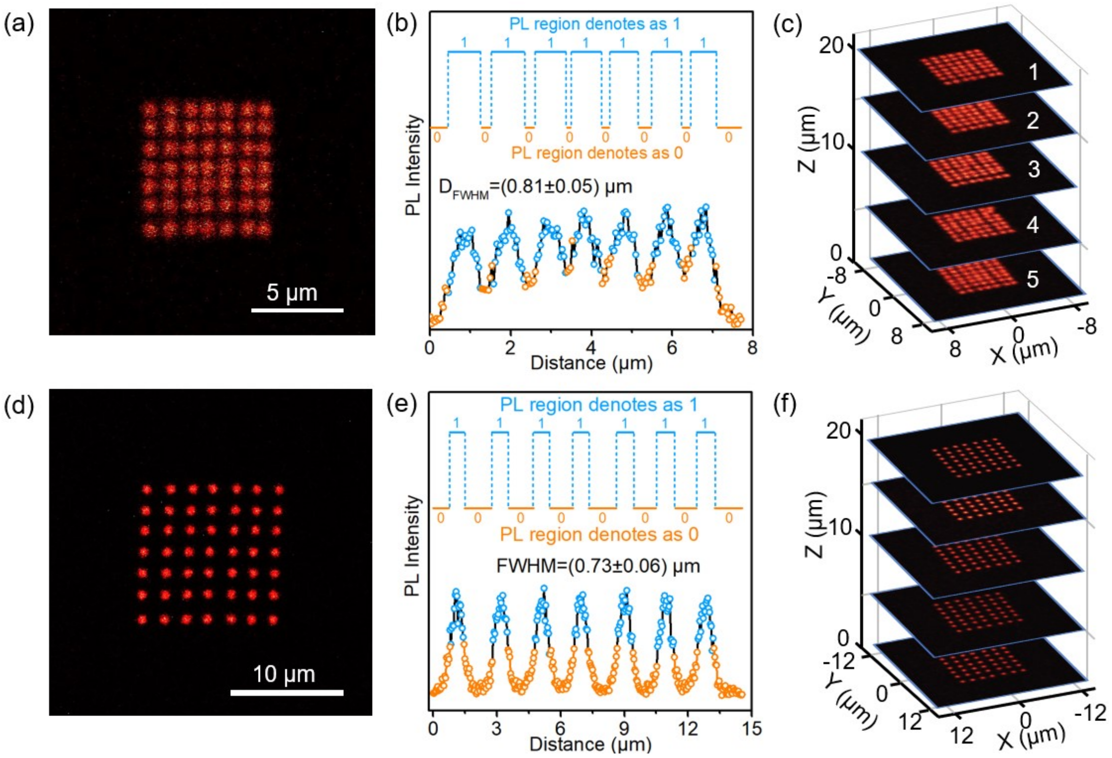

Figure S8. (a,c) 7×7 arrays written by a 19 nJ femtosecond laser with an intervals of 1 µm and 2 µm, respectively. (b,e) Intensity profile along the horizontal direction of the array, realizing the “0” and “1” state change in binary information. (c,f) Three-level stack of five 7×7 matrix with an interval of 5 µm.

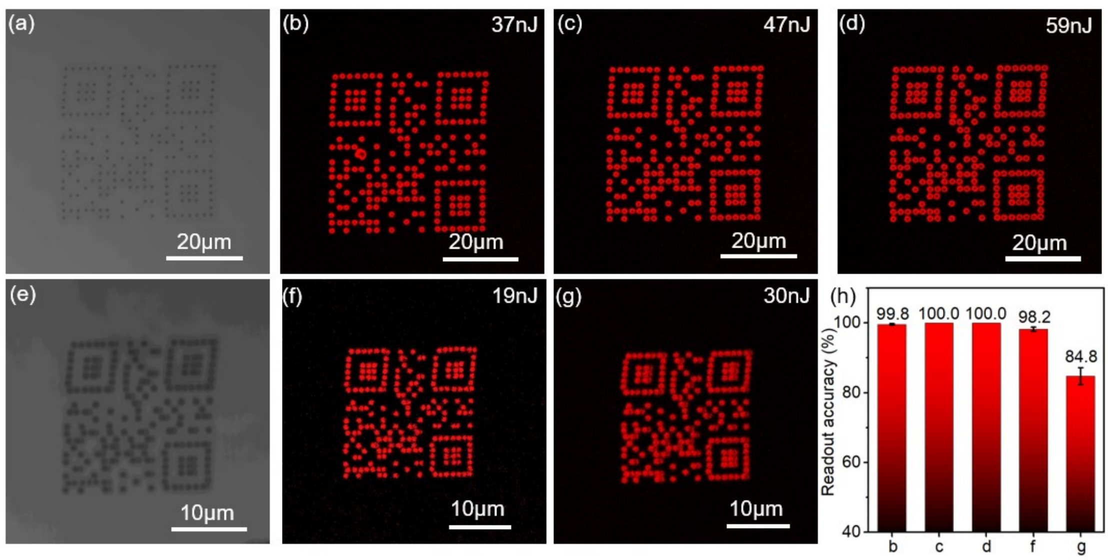

Figure S9. Bright-field images (a; d) and confocal fluorescence images (b; c; d; f; g) of QR codes with the interdomain distance of 2µm in G5 glass through direct writing with different fs laser energies (labelled on each images). Information readout accuracies, (h), of each fs laser written QR codes.

Supplementary Note 1

Eleven pre-prepared G5 glass samples are processed using a femtosecond laser to fabricate five lines segments at a depth of 50 μm. The processing parameters are 169 fs, 1 kHz, and 50 nJ, with a scanning speed of 50 μm/s for the laser lines. Confocal microscopy is used to observe and measure the fluorescence intensity of the processed lines. The eleven glass samples are then heat-treated at the following conditions: 623 K for 12, 24, and 48 hours; 673 K for 2, 4, and 8 hours; 773 K for 1, 2, and 3 hours; and 873 K for 0.25 and 0.5 hours in Figure S6 (a). Except for the glass treated at 873 K for 0.5 h, which exhibits a slightly yellowish surface, all other glass samples remained colorless and transparent. The experiments assume that the thermal activation-induced decay time (τ) of the silver cluster luminescence follows the Arrhenius law[2, 3], depending on temperature (T):

$$\frac{1}{\tau} = A \cdot exp\left(\frac{E_a}{K_B T}\right)$$

where E_a is the activation energy for the transformation of luminescent silver clusters into non-luminescent silver nanoparticles, and K_B is the Boltzmann constant. After heat treatment, the fluorescence intensity of the glass was measured and compared with that before heat treatment. The fluorescence lifetime of the emission center at 623 K, 673 K, 773 K, and 873 K is as fitted in Figure S6 (b). These lifetime values are then inserted into the Arrhenius equation, with 1/T on the x-axis and ln(1/τ) on the y-axis, to fit the fluorescence lifetime of the emission center at room temperature. Through laser confocal mapping, it is observed that the fluorescence in G5 glass almost disappeared after heat treatment at 873 K for 0.5 h. This indicates that the information written by the laser has been erased. The glass, however, remains transparent, facilitating subsequent information rewriting.

Reference

1. X. Li, Y. Wang, P. Yang, T. Han, X. Shi, K. He and C. Zu, *Journal of Non-Crystalline Solids*, 2022, **596**.
2. Z. Wang, B. Zhang, D. Tan and J. Qiu, *Opto-Electronic Advances*, 2023, **6**, 220008-220008.
3. A. S. Lipatiev, S. S. Fedotov, S. V. Lotarev, T. O. Lipateva, G. Y. Shakhgildyan and V. N. Sigaev, *ACS Applied Nano Materials*, 2022, **5**, 6750-6756.