

Glass network engineering enables efficient nir cut-off in Cu²⁺ blue glasses

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Abstract: Near-infrared (NIR) cut-off filters play a key role in imaging systems by blocking NIR interference on CMOS sensors, thereby preventing image ghosting and distortion. However, current commercial Cu^{2+} -doped blue glasses struggle to balance high visible transmittance with complete NIR cut-off because of the uncontrolled formation of Cu^+ and Cu^{2+} and the difficulty of regulating the Cu^{2+} ligand field. Herein, we propose a network-engineering strategy to modify the fluorophosphate glass network through alkali-metal (AM) doping. Large-size AM ions in the glass provide high optical basicity and an oxidizing atmosphere, resulting in a $\text{Cu}^{2+}/\text{Cu}^+$ ratio as high as 29.87. Meanwhile, they regulate the glass network structure to reduce the octahedral distortion of the CuO_4F_2 unit, leading to a redshift of the NIR cut-off wavelength. As a result, the as-prepared blue glass exhibits both high visible transmittance and efficient NIR cut-off, outperforming commercial counterparts. Images captured using the present blue glass show higher saturation and more realistic color reproduction without NIR-light interference. This work provides a new strategy for addressing key bottlenecks in commercial blue glasses and offers an alternative material for advanced imaging.

Keywords: fluorophosphate glass; copper ions; optical basicity; glass filter; ligand field.

1 Introduction

With the widespread adoption and upgrading of camera equipment, performance requirements in diverse environments have become increasingly demanding. Eliminating NIR-light interference in imaging systems has therefore become a major challenge [1]. In this context, NIR cut-off glass filters, which efficiently transmit visible light while blocking NIR light, can effectively mitigate the adverse impact of NIR light on imaging systems and have been widely used as core components in digital cameras, surveillance cameras, and smartphones [2-6]. Currently, the dominant NIR cut-off filter products are fabricated by depositing NIR-reflective films on highly transparent quartz glass [7]. However, multiple reflections and refractions of incident light among optical lenses can generate ghost images and light spots [8-12] (**Fig. S1**).

As an alternative, absorption-type NIR cut-off filters, represented by specially designed transition-metal (TM)-doped glasses, have rapidly emerged as promising solutions for next-generation imaging systems because of their low cost, simple processing, and their ability to address the limitations of traditional filters [13,14]. Among them, Cu^{2+} -doped fluorophosphate glasses, known as **blue glasses** (BG), have attracted considerable research interest. In general, the Cu^{2+} : $3d \rightarrow 3d$ transition gives rise to NIR absorption, whereas the associated Cu^{+} : $3d^{10} \rightarrow 3d^9 4s^1$ transition produces violet-blue absorption, which markedly reduces visible-light transmittance [15], and can additionally give rise to blue-to-green luminescence typically centered at 450-550 nm via the reverse $3d^9 4s^1 \rightarrow 3d^{10}$ transition [16-18]. In addition, the light-absorption characteristics strongly depend on the octahedral distortion of Cu^{2+} in the glass, which greatly affects the spectral region of Cu^{2+} NIR absorption [19,20]. Current research has mainly focused on the changes in the glass network structure induced by Cu ion introduction and the regulation of absorption behavior by crystal field strength.

However, the NIR absorption of Cu^{2+} -doped fluorophosphate glass is also affected by thickness (**Fig. S2**). To date, no studies have systematically explored how to achieve better performance at low thickness (0.21 mm, compatible with most commercial lenses). Therefore, achieving high visible-light transmittance ($T_{400 \text{ nm}}$ (transmittance at 400 nm) $\geq 85\%$ and λ_{T50} (wavelength at 50% transmittance) $> 660 \text{ nm}$) and NIR cut-off ($T_{1100 \text{ nm}}$ (transmittance at 1100 nm) $< 2\%$) (**Note S1**) requires both a high $\text{Cu}^{2+}/\text{Cu}^+$ ratio and a suitable crystal field that enables strong NIR absorption by Cu^{2+} .

Herein, we report innovative fluorophosphate glasses with both high $\text{Cu}^{2+}/\text{Cu}^+$ ratios and appropriate crystal fields by regulating the glass network through alkali-metal (AM = Li^+ , Na^+ , K^+ , Rb^+ , Cs^+) doping. AM ions with large radii are shown to provide higher optical basicity, which effectively suppresses $\text{Cu}^{2+} \rightarrow \text{Cu}^+$ reduction [21], thereby enhancing visible-light transmittance and strengthening NIR cut-off. Meanwhile, AM dopants modify the glass network structure and reduce the octahedral distortion of the CuO_4F_2 unit, leading to a redshift of the NIR cut-off wavelength [22]. Consequently, a desirable blue glass with $T_{400 \text{ nm}}$ of 85%, λ_{T50} of 669 nm, and $T_{1100 \text{ nm}} < 2\%$ is achieved. Compared with a commercial blue glass such as HOYA CXA700, the developed blue glass exhibits better color reproduction in outdoor imaging and superior performance under varying illumination conditions throughout the day.

2 Experimental

2.1 Materials

Glass samples with nominal compositions of $55\text{NH}_4\text{H}_2\text{PO}_4\text{-}10\text{M}_2\text{CO}_3\text{-}20\text{NH}_4\text{F-}10\text{CuO-}1\text{Al}_2\text{O}_3\text{-}1\text{Y}_2\text{O}_3\text{-}3\text{BaF}_2$ (M = Li, Na, K, Rb, Cs; mol%) were prepared via a melt-quenching method. The raw materials included

NH₄H₂PO₄ (Maclean, 99.9%), Li₂CO₃ (Maclean, 99.9%), Na₂CO₃ (Maclean, 99.9%), K₂CO₃ (Maclean, 99.9%), Rb₂CO₃ (Maclean, 99.9%), Cs₂CO₃ (Maclean, 99.9%), NH₄F (Maclean, 99.99%), CuO (Aladdin, 99.99%), Al₂O₃ (Maclean, 99%), Y₂O₃ (Maclean, 99.99%), and BaF₂ (Maclean, 99.99%). The compound powders, with a total mass of 10-150 g, were weighed, mixed, and thoroughly ground in an agate mortar for 20 min. Subsequently, the well-mixed powders were placed in an alumina crucible and melted in a muffle furnace at 1100°C for 1 h. The molten glass was then poured onto an iron plate preheated to 300°C for shaping and quickly transferred to a muffle furnace at 350°C for 10 h to eliminate internal stress (**Fig. S3**). Finally, after cooling to room temperature, a blue-green transparent sheet-like glass was obtained, cut, and ground to a uniform size for further use.

2.2 Characterizations

X-ray diffraction (XRD) patterns of the samples were collected using an X-ray diffractometer (D8, Bruker, Germany) equipped with Cu-K α radiation ($\lambda = 1.5406 \text{ \AA}$) operated at 40 kV and 30 mA. The elemental distribution characteristics of the samples and the average valence state of Cu ions were characterized using a double-image-difference-corrected transmission electron microscope (2AC-TEM; Spectra300, Thermo Fisher, America), and electron energy loss spectroscopy (EELS) was recorded using an attached spectrometer. To characterize the transmittance performance of the blue glass, transmittance spectra were measured using a UV-visible-near-infrared spectrophotometer (Cary-500, Agilent Technologies, America). Fourier transform infrared spectroscopy (FTIR; VEC-TOR33, Bruker, UK) and Raman spectroscopy (DXR2xi, Thermo Fisher, America) were used to examine the vibrational behavior of the samples. X-ray photoelectron spectroscopy (XPS) data were obtained using an XPS instrument (K-Alpha, Thermo Scientific, America) to

determine elemental valence states and composition. The quantitative analysis of Cu^{2+} was performed using the Avantage software, and we adopted a combined main-peak plus satellite-peak fitting strategy to determine the total contribution of Cu^{2+} . To obtain the valence state and coordination environment of Cu ions, X-ray absorption near-edge structure (XANES) and X-ray absorption fine structure (EXAFS) tests were carried out using a synchrotron-radiation instrument (RapidXAFS 2D Ultra, RapidXAFS, China). The electron paramagnetic resonance (EPR) spectrum was measured using a paramagnetic resonance spectrometer (EMXplus-6/1, Bruker, Germany) at room temperature. To characterize the solar-light spectrum under different filter conditions (BG, CXA700, and 800 nm cut-off filter), data were collected using a high-resolution spectrometer (HR-6XR300-25, Ocean Optics, America). To determine the elemental composition and fluorine retention, inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5800 ICP-OES, Agilent, America) and ion chromatography (IC, Thermo Scientific ICS-600, Thermo Scientific, America) analyses were performed, respectively. The mass percentage of oxygen was calculated by the difference method, i.e., subtracting the sum of the mass percentages of all other measured elements from 100%. To determine the thermal behavior and weight loss, differential thermal analysis (DTA, STA449F3, Netzsch, Germany) and thermogravimetric analysis (TG, STA449F3, Netzsch, Germany) analyses were performed, respectively.

3 Results and discussion

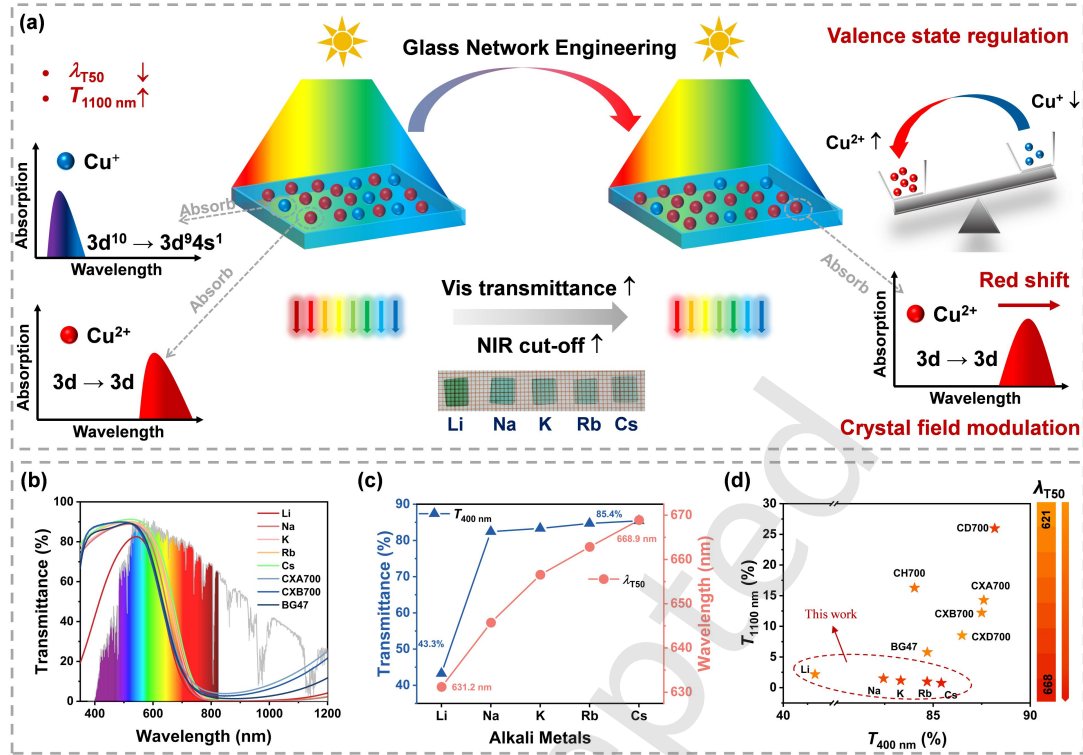


Fig. 1 (a) Schematic illustration of network engineering for achieving high visible-light transmittance and NIR cut-off in fluorophosphate glass via AM doping. (b) Transmission spectra of fluorophosphate glasses doped with different AM ions (Li^+ , Na^+ , K^+ , Rb^+ , Cs^+), several typical commercial CXA700, CXB700 and BG47 blue glasses, all with a thickness of 0.21 mm, together with the solar spectrum (AM1.5G). (c) Comparison of $T_{400 \text{ nm}}$ and λ_{T50} for samples with the same thickness of 0.21 mm. (d) Comparison of $T_{400 \text{ nm}}$, $T_{1100 \text{ nm}}$, and λ_{T50} between the fluorophosphate glasses and commercial blue glasses (all thicknesses: 0.21 mm or 0.20 mm).

3.1 Comparison of NIR cut-off performance

As shown in **Fig. 1(a)**, copper ions in fluorophosphate glass generally coexist as Cu^+ and Cu^{2+} . To achieve both high visible transparency and NIR cut-off, it is necessary to increase the $\text{Cu}^{2+}/\text{Cu}^+$ ratio while reducing the crystal-field strength of Cu^{2+} , thereby promoting a redshift of Cu^{2+} absorption. Herein, AM dopants are introduced into specially designed fluorophosphate glass to modify its topological structure (**Fig. 1(a)**). The glass color gradually changes from emerald green to sky blue as the AM ionic radius increases, which is attributed to the gradual decrease in Cu^+ absorption in the visible region.

X-ray diffraction (XRD) shows no distinct crystalline diffraction peaks, confirming the amorphous nature of the material (**Fig. S4**). High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) analysis (**Fig. S5**) verifies that the elements are uniformly distributed in the sample. **Figs. 1(b)** and **1(c)** show the transmission spectra and the comparison of $T_{400 \text{ nm}}$ and λ_{T50} , confirming that, as the radius of the doped AM ions increases, $T_{400 \text{ nm}}$ increases from 43.3% to 85.4%, λ_{T50} redshifts from 631.2 nm to 668.9 nm, and $T_{1100 \text{ nm}}$ decreases from 2.2% to 0.8% (**Fig. S6**). This suggests that large-radius AM ions are beneficial for inhibiting Cu^+ formation and promoting the absorption redshift of Cu^{2+} ions. **Fig. 1(d)** presents a comparison of the performance of the as-prepared glasses with that of commercial Cu^{2+} -doped blue glasses. The data clearly demonstrate that the present glasses exhibit comparable $T_{400 \text{ nm}}$ transmittance in the visible spectral region but markedly better $T_{1100 \text{ nm}}$ and λ_{T50} NIR cut-off performance in the NIR region, outperforming the commercial counterparts (**Table 1**).

Table 1 Comparison of the properties ($T_{400 \text{ nm}}$, $T_{1100 \text{ nm}}$, and λ_{T50}) of the present AM-doped fluorophosphate glasses with those of commercial blue glasses (all compared commercial data are taken from manufacturer datasheets).

Sample	$T_{400 \text{ nm}}$ (%)	$T_{1100 \text{ nm}}$ (%)	λ_{T50} (nm)	Company	Thickness
CXD700	86.5	8.5	621	HOYA	0.20 mm
CXA700	87.6	14.3	632	HOYA	0.21 mm
CXB700	87.5	12.21	627	HOYA	0.21 mm
CH700	84.0	16.3	633	HOYA	0.21 mm
CD700	88.2	25.9	653	HOYA	0.20 mm
BG47	84.7	5.8	632	SCHOTT	0.21 mm
Li	43.3	2.2	631	This work	0.21 mm
Na	82.4	1.5	645	This work	0.21 mm
K	83.3	1.2	656	This work	0.21 mm
Rb	84.7	1.0	662	This work	0.21 mm
Cs	85.4	0.8	669	This work	0.21 mm

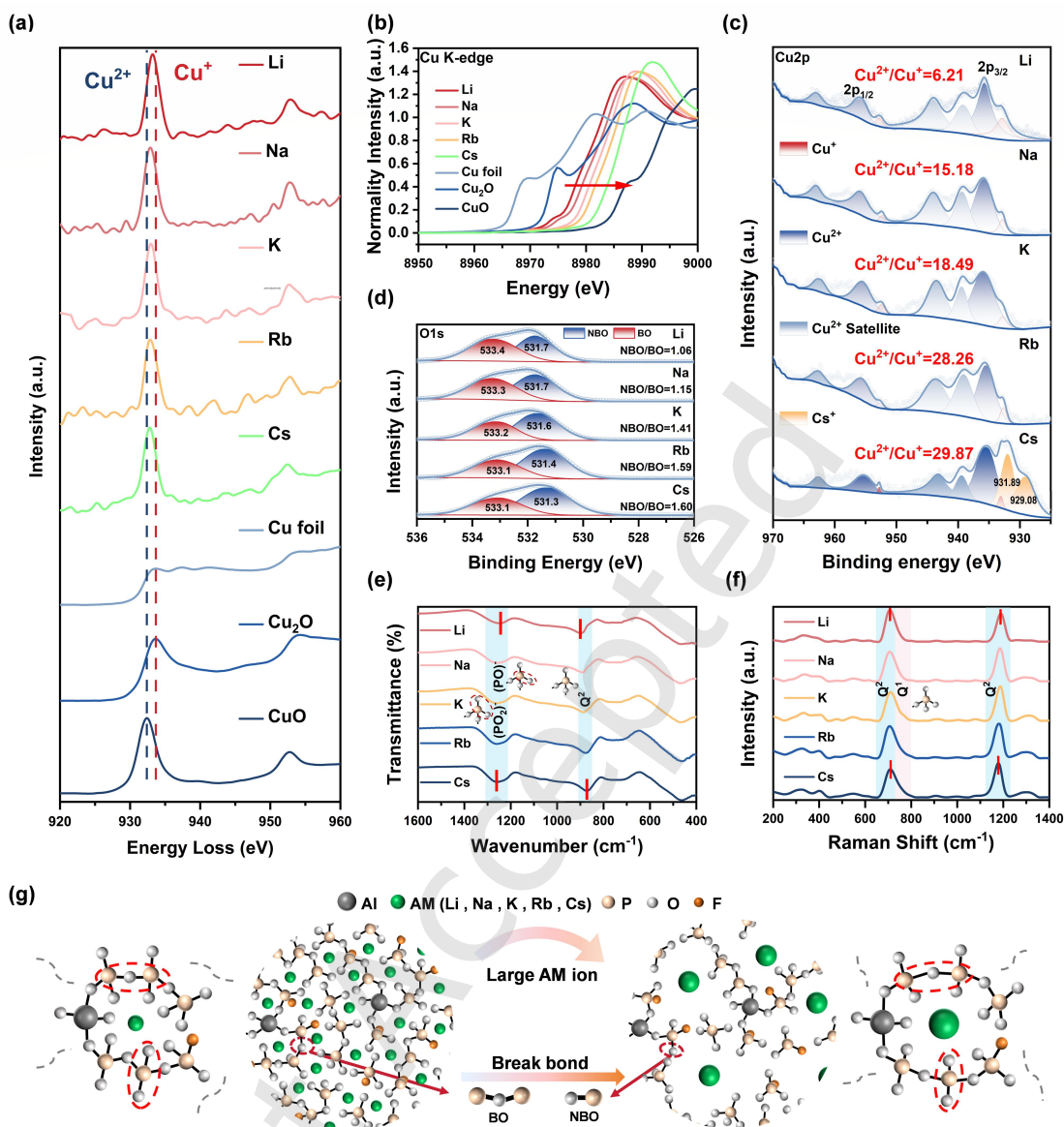


Fig. 2 (a) STEM-EELS spectra, (b) XANES spectra, high-resolution XPS profiles of (c) Cu 2p and (d) O 1s, (e) FTIR spectra, and (f) Raman spectra (532 nm excitation) of the as-prepared blue glasses. (g) Schematic diagram of the glass network structure modified by AM dopants.

3.2 Characterization of the glass network structure

XPS analysis was used to identify the elemental composition and relative contents in the samples. The actual composition determined by ICP-OES and IC is close to the nominal composition (**Table S1**), with the minor deviation attributed to volatilization during melting. As shown in **Fig. S7**, all expected elements are detected in the glass. EELS analyses (**Fig. 2(a)**) further reflect the average valence state of

copper ions. The peak positions of all samples lie between those of Cu₂O (Cu⁺) and CuO (Cu²⁺), indicating that the Cu ions have an average positive valence state between +1 and +2 (**Table S2**). Moreover, as the radius of the AM ions increases, the peak position gradually shifts toward lower energy loss, indicating that the average valence state continuously increases and that the proportion of Cu²⁺ relative to Cu⁺ rises monotonically [23-25]. This trend is further confirmed by XANES data. As shown in **Fig. 2(b)**, the near-edge absorption shifts toward higher energy, indicating an increase in the average valence state of the sample [26]. The Cu²⁺/Cu⁺ proportion was quantitatively analyzed from the Cu 2p XPS spectra (**Fig. 2(c)**, **Note S2**). As the AM dopant changes from Li⁺ to Cs⁺, the ratio of Cu²⁺ (~935 eV) to Cu⁺ (932 eV) gradually rises from 6.21 to 29.87 [27], far exceeding the 3.61 of the commercial blue glass CXA700 (**Fig. S8**). Here, two additional broad peaks (929.08 eV and 931.89 eV) in the Cs-containing XPS profile are attributed to peaks of Cs (**Fig. S9**). These results confirm that the proportion of Cu²⁺ relative to Cu⁺ continuously increases in the present blue glass as the AM dopant changes from Li⁺ to Cs⁺. This is ascribed to the fact that, as the ionic radius increases, the ability of the AM ion to bind surrounding electron clouds weakens, enhancing the electron-pair-donating ability of the glass system and thereby increasing the optical basicity [28-30]. As listed in **Table S3**, the theoretical optical basicity rises from 0.6354 to 0.7601 as the AM ion changes from Li⁺ to Cs⁺. Under identical oxygen partial pressure during melting, higher optical basicity is beneficial for creating a more oxidative environment, thereby suppressing Cu⁺ formation and increasing the proportion of Cu²⁺ in the present glass. Increasing AM content enhances optical basicity and promotes Cu²⁺ formation, thereby improving visible transmittance and strengthening NIR cut-off capability, but excessive AM deteriorates mechanical strength and chemical stability (**Fig. S10**).

Therefore, 10 mol% is selected as the optimal concentration to balance optical performance and material stability.

To investigate changes in the glass network structure after the introduction of different AM ions, O 1s XPS, FTIR spectroscopy, and Raman spectroscopy were performed. **Fig. 2(d)**, **Fig. S11** and **Table S4** show the O 1s XPS profiles, illustrating changes in the relative contents of bridging oxygen (BO, ~531 eV) and non-bridging oxygen (NBO, ~533 eV) [31]. With increasing AM ionic radius, the NBO/BO ratio rises from 1.06 to 1.60. This is attributed to the weakened polarizing power of larger AM ions, which reduces their attraction to O^{2-} electron clouds [28,32], which converts P-O-P BO bonds into P-O-M NBO bonds and leads to a looser glass network structure. As shown in **Fig. 2(e)**, **Fig. S12**, and **Table S5**, with increasing AM radius, the signals in the 1243-1273 cm^{-1} range, assigned to the symmetric stretching vibrations of NBO ($(P-O)^-$ and $(PO_2)^-$ in the Q^2 unit, shift toward higher wavenumber, indicating that the NBO bond lengths in both units gradually shorten [33-35]. The vibration band in the 875-903 cm^{-1} range originates from the symmetric stretching vibration of the BO (P-O-P) bond in the Q^2 unit and shifts toward lower wavenumber, indicating that the BO (P-O-P) bond length continuously increases [36]. Similar results are observed in the Raman spectra (**Fig. 2(f)**, **Fig. S13**, and **Table S6**), where the BO signal in the Q^2 unit (702-709 cm^{-1}) shifts toward lower wavenumber, whereas the NBO signal in the Q^2 unit (1184-1258 cm^{-1}) shifts toward higher wavenumber. In addition, the symmetric stretching vibration intensity assigned to the P-O-P bond in the Q^1 unit (765-777 cm^{-1}) gradually increases [37-39], confirming that the number of Q^1 units continuously increases, thereby making the glass structure more "loose". **Fig. 2(g)** schematically illustrates the alteration of the glass network structure induced by AM dopants. Generally, AM ions occupy the interstitial spaces of the fluorophosphate

glass network, and larger ions cause the glass network to expand, which in turn increases the P-O-P BO bond length. Furthermore, in the P-O-M structure, the electronegativity difference of the P-O bond is significantly smaller than that of the M-O bond (**Table S7**), causing the covalency of the P-O bond to increase as the ionicity of the M-O bond increases [40,41]. Therefore, compared with the Li-O bond, the Cs-O bond has greater ionicity, and the corresponding P-O NBO bond exhibits higher covalency and a correspondingly shorter bond length. Although larger alkali ions expand the network, density still rises from Li to Cs due to the dominant mass effect (**Fig. S14**) [42].

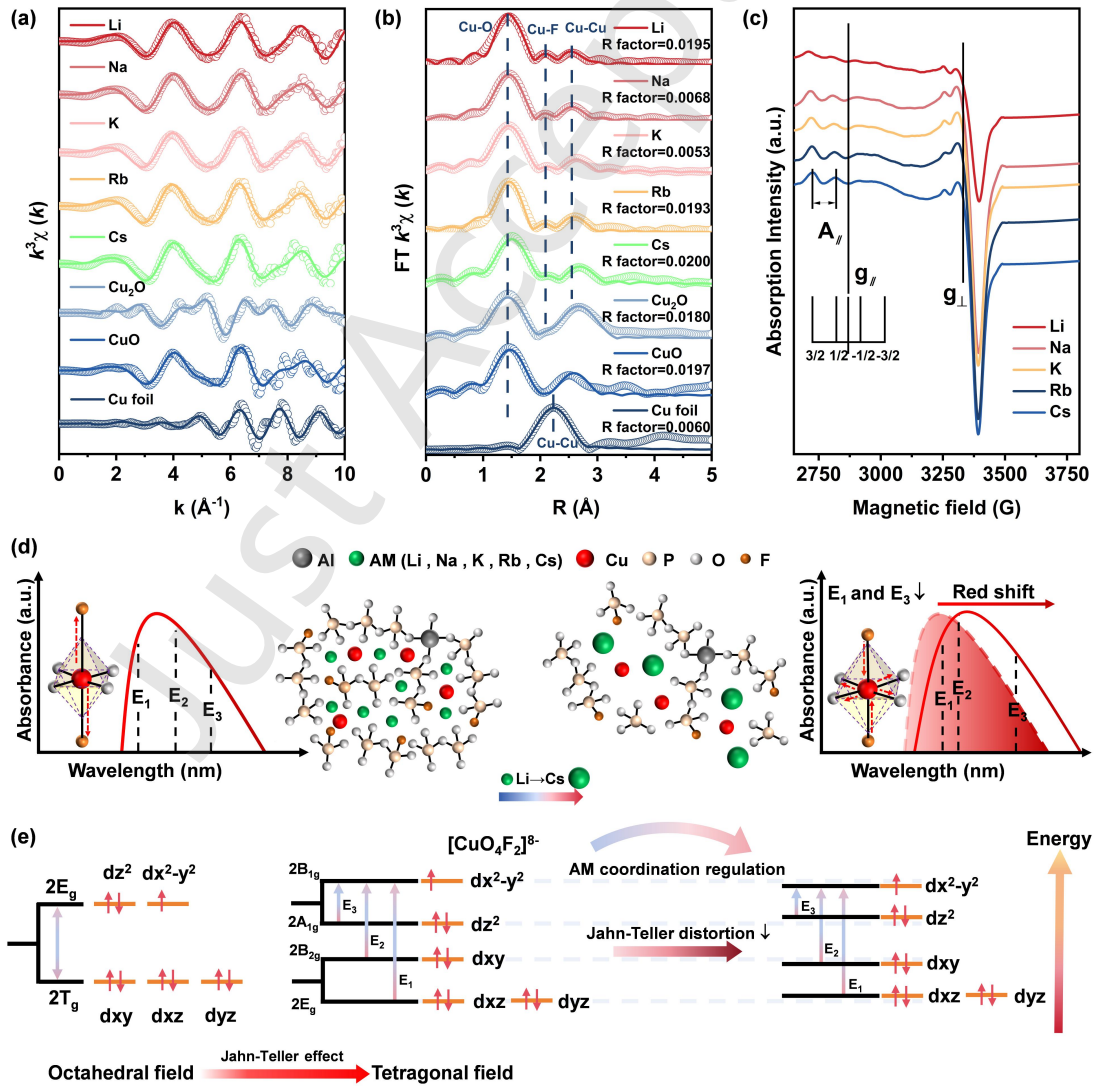


Fig. 3 (a) k^3 -weighted Cu K-edge EXAFS spectra, (b) Cu K-edge Fourier-transform EXAFS

spectra, and (c) Room-temperature EPR spectra of the present blue glasses doped with different AM ions. (d) Schematic diagram of the AM-modified glass network and its influence on the $[\text{CuO}_4\text{F}_2]^{8-}$ unit along the typical Z^2 axis. (e) Energy-level transitions of Cu^{2+} ions.

3.3 Ligand field of Cu^{2+} ions and redshift of NIR absorption

To further explore the chemical states and local coordination environments of Cu^{2+} ions, EXAFS analyses were conducted on blue glasses doped with various AM ions (**Fig. 3(a)**). The k^3 -weighted fitting of the Cu K-edge EXAFS data in k space shows good overall agreement with the experimental spectra (**Fig. 3(a)**). Fitting of the EXAFS spectra in R space indicates three main shells (**Fig. 3(b)**): the first shell corresponds to the Cu-O bond, the second to the Cu-F bond, and the third to the Cu-Cu bond. The fitted structural parameters are provided in **Table S8-10**. These spectra were well fitted (R factor ≤ 0.02), with fitted coordination numbers (CNs) of approximately 4 and 2 for the Cu-O and Cu-F bonds, respectively. Therefore, these results indicate that Cu^{2+} exists in a six-coordinate form in the AM-doped fluorophosphate glasses, with 4 O^{2-} and 2 F^- as the nearest neighbors, i.e., in the $[\text{CuO}_4\text{F}_2]^{8-}$ unit. Importantly, with increasing AM ionic radius, the Cu-O bond length increases from 1.94 Å to 1.97 Å, while the Cu-F bond length decreases from 2.18 Å to 2.15 Å (**Table S8**). The corresponding wavelet transform spectra (**Fig. S15**) further illustrate the variation in Cu-O and Cu-F bond lengths.

For Cu^{2+} with a $3d^9$ configuration and an unpaired electron, EPR spectroscopy is an effective technique for analyzing its local structure (**Fig. 3(c)**). Here, the $g_{\parallel}$, $g_{\perp}$, and $A_{\parallel}$ parameters are used to evaluate the degree of local ligand distortion (**Note S3**). As listed in **Table S11**, both $g_{\parallel}$ and $g_{\perp}$ are greater than the free-electron g_e ($g_{\parallel} > g_{\perp} > g_e = 2.0036$), indicating that the $[\text{CuO}_4\text{F}_2]^{8-}$ unit undergoes

Z^2 -axial-stretching-type octahedral distortion [43,44]. Increasing the AM ionic radius affects the spin-Hamiltonian parameters, leading to an increase in $g_{\perp}$ and $A_{//}$ and a decrease in $g_{//}$ (**Table S11**). Generally, the $g_{//}/A_{//}$ ratio is used to evaluate the degree of octahedral distortion [45,46]. As shown in **Fig. S16**, the $g_{//}/A_{//}$ ratio monotonically decreases from 278 cm to 252 cm with increasing AM ionic radius, verifying that the degree of $[\text{CuO}_4\text{F}_2]^{8-}$ octahedral distortion gradually decreases.

Based on the EXAFS and EPR results, **Fig. 3(d)** illustrates the variation in glass network structure, the $[\text{CuO}_4\text{F}_2]^{8-}$ octahedron, and NIR absorption upon AM doping. When AM dopants with large ionic radii are introduced as modifiers into the glass network, the Cu-F bond length along the Z^2 axis in the $[\text{CuO}_4\text{F}_2]^{8-}$ octahedron shortens, while the Cu-O bond length on the equatorial (X^2 , Y^2) axes elongates. Consequently, the bond-length difference between the Z^2 axis and the (X^2 , Y^2) axes is reduced, ultimately lowering the tensile distortion of the $[\text{CuO}_4\text{F}_2]^{8-}$ octahedron along the Z^2 axis and resulting in a redshift of Cu^{2+} NIR absorption (**Fig. 3(d)**). As schematically shown in **Fig. 3(e)**, the triplet state $2E_g$ and the doublet state $2T_g$ of Cu^{2+} ($3d^9$) in an octahedral field split into $2B_{1g}$ and $2A_{1g}$ and into $2B_{2g}$ and $2E_g$, respectively, because of stretching distortion along the Z^2 axis of $[\text{CuO}_4\text{F}_2]^{8-}$ (i.e., the Jahn-Teller effect). The $2E_g \rightarrow 2B_{1g}$ (E_1), $2B_{2g} \rightarrow 2B_{1g}$ (E_2), and $2A_{1g} \rightarrow 2B_{1g}$ (E_3) transitions contribute to NIR absorption, where E_2 mainly depends on the ligand type and E_1 and E_3 are related to the degree of octahedral distortion [47-49]. As the AM ion changes from Li^+ to Cs^+ , the decreased octahedral distortion weakens the Jahn-Teller effect and reduces the energy-level splitting between $2B_{1g}$ and $2A_{1g}$ as well as between $2B_{2g}$ and $2E_g$, thereby decreasing E_1 and E_3 and redshifting Cu^{2+} NIR absorption. Therefore, compared with other alkali metals, only Cs^+ -doped blue glass can simultaneously achieve high visible transmittance and deep NIR cut-off.

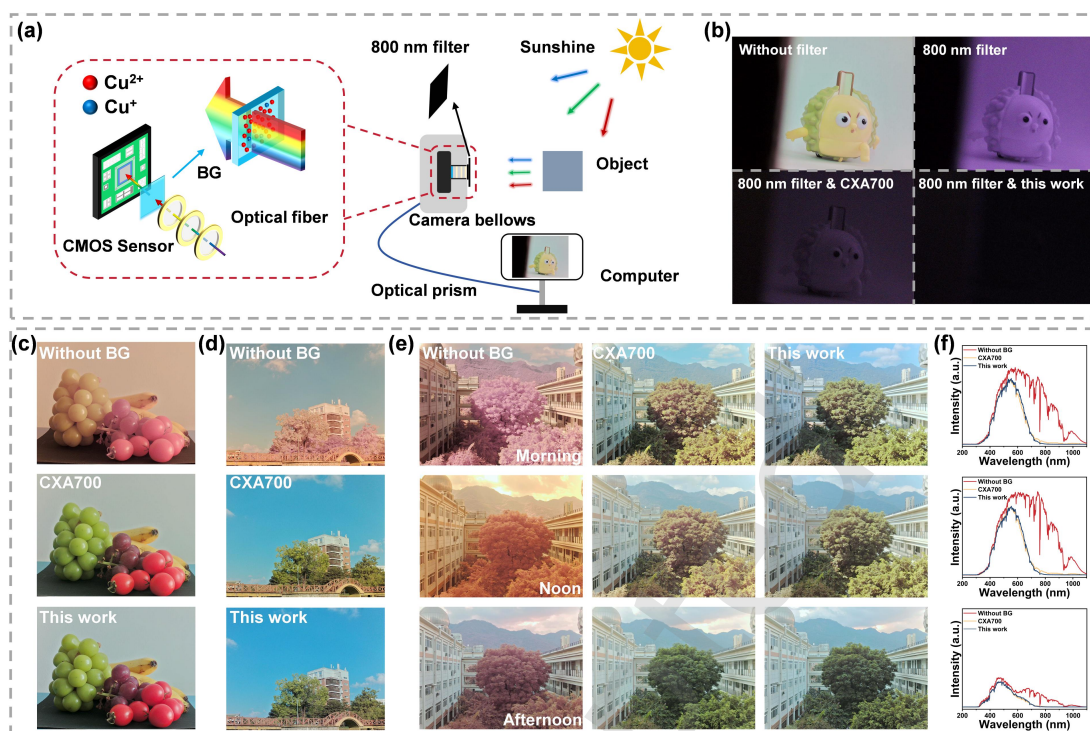


Fig. 4 (a) Schematic diagram of the residual NIR-light detection system. (b) Images captured by the CMOS sensor without a filter, with an 800 nm cut-off filter, and with a blue glass (commercial CXA700 or the investigated glass, both with a thickness of 0.21 mm). Images of (c) fruits and (d) outdoor scenery taken without/with blue glasses (BG, both with a thickness of 0.21 mm). (e) Comparison of outdoor scenery images captured in the morning, at noon, and in the afternoon, and (f) the corresponding solar spectra with/without blue glasses (BG, both with a thickness of 0.21 mm).

3.4 Imaging application

Finally, we demonstrate the practical application of the as-prepared blue glass in an imaging system. The as-prepared blue glass is suitable for large-scale industrial production in various sizes (**Fig. S17**), and it shows excellent mechanical properties (**Fig. S18**) and uniform light transmission (**Fig. S19**). Durability tests, including thermal cycling, moisture resistance, and acid resistance, were performed (**Fig. S20**). The Cs-doped blue glass exhibits stable optical performance after 25-100 thermal cycles between 30 and 120 °C and superior acid resistance to commercial CXA700 (25% HCl at 50 °C for 1 h). Although slight hydrolysis occurs in water at 50 °C due

to the intrinsic susceptibility of phosphate glass, encapsulation by coating films on the sides and top/bottom surfaces can effectively isolate moisture and oxygen, ensuring long-term stability in practical applications. A fiber-optic spectrometer (**Fig. S21**) is designed to compare the NIR absorption ability of the present blue glass with that of commercial CXA700. Using an 800 nm filter and the fiber-optic spectrometer, the present blue glass exhibits no detectable NIR signal, in contrast to CXA700, which shows a residual NIR signal (**Fig. S22**). Furthermore, a direct imaging system for residual NIR light is constructed (**Fig. 4(a)**). When only the 800 nm filter is used, the CMOS sensor captures an image induced by the NIR signal, and the image remains detectable after commercial CXA700 is added. In contrast, the image becomes completely invisible when the present blue glass is used, demonstrating its superior NIR cut-off performance compared with the commercial glass (**Fig. 4(b)**).

Under identical exposure, ISO, aperture, white balance, and image processing parameters, images of fruits (**Fig. 4(c)**) and outdoor scenery (**Fig. 4(d)**) captured with the present blue glass show higher saturation and more realistic color reproduction than those captured with commercial CXA700, without NIR light interference. We further conducted color-fidelity tests at different times of day (morning, noon, and afternoon), as shown in **Fig. 4(e)**. The solar spectral intensity varies among morning, noon, and afternoon (**Fig. 4(f)**, **Fig. S23** and **Table S12**). Under high solar-intensity conditions in the morning and at noon, the present blue glass suppresses NIR interference in imaging more effectively than CXA700 (**Fig. 4(f)**, **Fig. S23** and **Table S12**), resulting in better image quality (**Fig. 4(e)**). Under low solar-intensity conditions in the afternoon, both blue glasses effectively block NIR light and yield satisfactory images. Therefore, the as-prepared blue glass exhibits better color-rendition performance than commercial CXA700 under various

ambient-lighting conditions. However, the high cost of Cs_2CO_3 still restricts low-cost mass production, whereas K-doped glass offers commercial-level performance at low cost, making it the most promising candidate for replacing commercial blue glass filters.

4 Conclusions

In summary, the topological structure of fluorophosphate glass is deliberately regulated by AM-ion doping to adjust the valence state of copper ions and the degree of $[\text{CuO}_4\text{F}_2]^{8-}$ octahedral distortion. Importantly, AM dopants with larger ionic radii provide higher optical basicity and help maintain an oxidative environment and a suitable crystal-field environment that reduces octahedral distortion. Consequently, a high $\text{Cu}^{2+}/\text{Cu}^+$ ratio and a redshift of Cu^{2+} NIR absorption are realized, leading to high visible transmittance ($T_{400\text{ nm}} = 85\%$) and efficient NIR cut-off ($\lambda_{\text{T}50} = 669\text{ nm}$, $T_{1100\text{ nm}} < 2\%$) for the as-prepared blue glass. As a proof of concept, a camera module assembled using CMOS sensors and the blue glass was designed; compared with a commercial blue glass, images captured with the as-prepared glass show higher saturation and more realistic color reproduction without NIR-light interference. This work provides a new strategy for addressing the performance limitations of commercial blue glasses and promotes their application in high-end photography.

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Author contributions

Z. Y. Hu and S. Y. Zhu performed most of the experiments and wrote the first draft. D. Chen helped analyze the experimental results and finalize the manuscript. S. S. Lin, T. Pang, L. W. Zeng, and F. Huang helped perform the spectroscopic measurements. D. Chen conceived the study and supervised the project. All authors discussed the results and commented on the manuscript.

Availability of data and materials

All data are available from the corresponding author upon request.

Competing interests

The authors have no competing interests to declare that are relevant to the content of this article.

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