Laser & Photonics Reviews / Volume 15, Issue 4 / 2000525

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First published: 01 February 2021
https://doi.org/10.1002/lpor.202000525

Highly Responsive Photochromic Ceramics for High Contrast Rewritable Information Displays

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Keywords: photochromic ceramic, $K_{0.5}Na_{0.5}NbO_3$, response time, coloration contrast, hand-rewritable display

Abstract

Inspired by their excellent thermal stability and strong fatigue resistance, inorganic photochromic materials have been highlighted as promising candidates in various photonic applications ranging from photo-switches, anti-counterfeiting and encryption to information storage. However, the lack of suitable inorganic materials with both fast photo-response and strong coloration contrast heavily restricts their applications. Herein, a new strategy is proposed to achieve high photochromic performance via constructing deep-lying traps in ferroelectric ceramics. The obtained $K_{0.5}Na_{0.5}NbO_3$-Eu (KNN-Eu) ceramic exhibits a reversible yellow-gray color change with high fatigue resistance upon alternating illumination (420 nm) and thermal stimulus (450 ℃). A fast response time of around 1 s and a large reflectivity difference of 39.2 % between the colored and bleached states are simultaneously achieved in KNN-Eu ceramic, which is by far the best performance ever reported in inorganic photochromic materials. Benefiting from these excellent properties, KNN-Eu is the first ferroelectric photochromic ceramic to support an instant and hand-(re)writable information display. The enhanced photochromic performance is expected to facilitate the application of photochromic materials in numerous optical devices and provides a significant guidance to design other inorganic photochromic materials.

1. Introduction

Photochromism is a reversible transformation of a chemical species between two states with different absorption spectra, induced in at least one direction by light irradiation. Using the optical difference between the two states, photochromic materials exhibit great potential for light-driven devices such as optical data storage, smart windows and rewritable copy paper.[1-4] For practical application, response time and coloration contrast are regarded as two key parameters of photochromic materials in addition to reversibility and stability.[5, 6] The coloration contrast (ΔR) can be evaluated from the reflectivity/transmittance difference before and after illumination. For photochromic materials, the coloration contrast usually increases rapidly in the initial irradiation stage and then changes slowly upon further irradiation, following an exponential-like behavior. Therefore, it is more meaningful for engineering applications to evaluate the required time to complete a large proportion rather than 100 % of the photochromic change. Based on this, the response time (t) is defined as the time required for the coloration variation to attain a (1- $^{1}/_{e}$) fraction or 63 % of the maximum value. A short response time endows photochromic materials for quick-responsive devices and real-time information recording, while high coloration contrast with a large signal-to-noise ratio is desirable for ultrasensitive devices. Meanwhile, good reversibility and stability ensure long-term and reliable operation of the corresponding devices. Therefore, great efforts have been made to develop photochromic materials with these functionalities.

Compared to organic photochromic materials, the merits of excellent thermal stability, long cycling life and stable chemical resistance make inorganic photochromic materials preferable for optical devices.[7] Currently, the extensively studied inorganic photochromic materials can be divided into three categories: transition metal oxides (TiO_2, WO_3, MoO_3, Nb_2O_5),[8-13] robust oxides ($BaMgSiO_4$, $Sr_3YNa(PO_4)_3F$, Sr_2SnO_4)[14-22] and ferroelectrics ($(K_{0.5}Nb_{0.5})NbO_3$ (KNN), $Na_{0.5}Bi_{4.5}Ti_4O_{15}$, $Na_{0.5}Bi_{2.5}Nb_2O_9$)[6, 23-28]. On the one hand, transition metal oxides usually possess a large coloration contrast but suffer from a slow response, poor reversibility, and weak chemical resistance. For example, the bleaching process of TiO_2 requires almost 15 min upon 365 nm illumination with a power density of 30 W m^{-2} in spite of a large coloration contrast.[11] Also, thermally bleached MoO_3 and WO_3 cannot be photo-colored again, showing low fatigability and poor chemical stability.[10, 29] On the other hand, robust oxides and ferroelectrics usually exhibit a fast response (< 2 min), while their coloration contrast is relatively small (< 25 %).[14, 23, 24, 26, 30, 31] For example, the maximum coloration contrast achieved in $Bi_{2.5}Na_{0.5}Nb_2O_9$: Pr, Er ceramic is only 22.5 % in spite of a fast response time of around 20 s.[31] To enhance the coloration contrast, Lv *et al*. and Jin *et al*. adopted co-doping with different rare earth ions to modulate the traps, and a coloration contrast enhancement from ~18 % to ~ 24 % was realized in $Sr_3GdNa(PO_4)_3F$: Eu ceramic via co-doping Pr.[15, 32] However, directly recording information with a portable laser is still difficult for these inorganic photochromic materials due to their slow photo-response or weak coloration contrast.[12, 14, 25] Thus, it is challenging to combine both fast response time and strong coloration contrast in inorganic materials to enable hand-writable information display.

The photochromic process in robust oxides and ferroelectrics is related to the trapping and de-trapping of charge carriers in vacancy-related defects, generated during the high-temperature sintering or through ion doping.[15, 17, 33] This trap-involved allows to regulate the photochromic performance via tailoring of the traps. Akiyama *et al*. found that doping with Fe^{3+} ions can significantly enhance the photochromism in $BaMgSiO_4$ due to the formation of deeper traps.[19] Also, an enhanced coloration contrast was achieved in $Sr_3YLi(PO_4)_3F$:Eu ceramic by co-doping with Ho^{3+} ions to generate deeper traps.[32] These results revealed that constructing deep-lying traps via suitable ion doping is an effective strategy for improving photochromism. Recently, KNN-based ceramics have attracted much research interest in photochromic application due to the relatively low phonon energy, high thermal resistance and good chemical stability.[34-37] Therefore, the benchmark KNN ceramic was selected as the matrix material to verify this strategy and both Al^{3+} and Eu^{3+} were introduced into KNN to tailor the traps. Compared to other doped KNN-based ceramics, the incorporation of Eu^{3+} ions generated deeper traps, resulting in both a fast response time of around 1 s and a strong coloration contrast of 39.2 %. Based on these excellent photochromic properties, recording information in real-time with a portable laser pen was realized in KNN-Eu ceramic, demonstrating a great potential in optical memory, anti-counterfeiting and photo-switching devices.

2. Results and Discussion

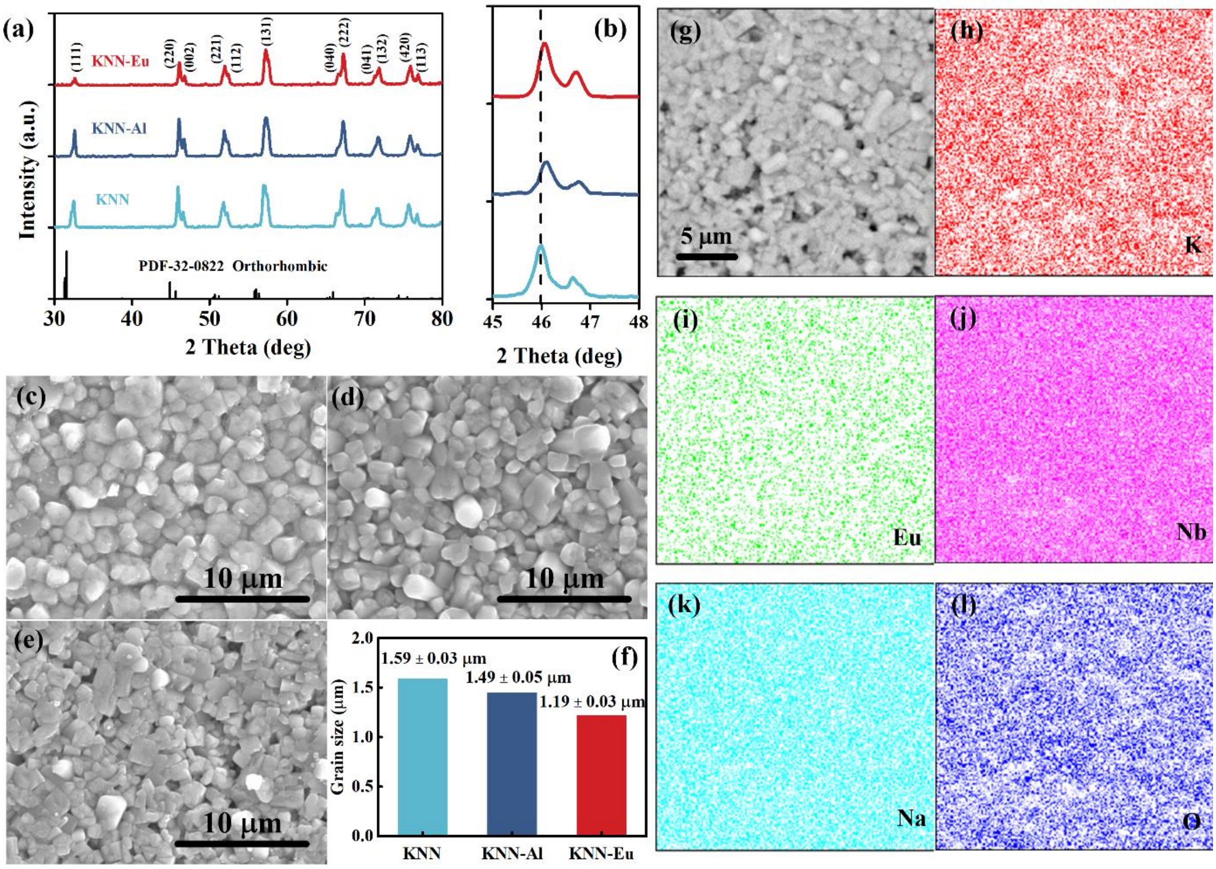

Figure 1. a) XRD patterns of KNN, KNN-Al and KNN-Eu ceramics. b) Zoomed area of XRD patterns in the 2θ range of 45°-48°. SEM images of c) KNN, d) KNN-Al and e) KNN-Eu ceramics. f) Average grain size of KNN-based ceramics. g)-l) SEM and corresponding elemental mappings of KNN-Eu ceramics.

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were employed to investigate the influence of Al^{3+} and Eu^{3+} doping on the microstructure of KNN ceramics. As shown in Figure 1a, a single perovskite structure with an orthorhombic phase was obtained for all ceramics, indicating that the Al^{3+} and Eu^{3+} dopant ions diffused into the KNN lattice. The reference pattern (PDF-32-0822) in the Figure 1a refers to $KNbO_3$, with a slightly larger lattice constant than KNN, explaining the systematic shift of all diffraction peaks. According to the ionic radius and coordination number of K^+ (1.64 Å, CN = 12), Na^+ (1.39 Å, CN = 12), Nb^{5+} (0.64 Å, CN = 6), Al^{3+} (0.53 Å, CN = 6) and Eu^{3+} (0.96 Å, CN = 12), Al^{3+} ions are expected to replace Nb^{5+} ions, while Eu^{3+} may enter the sites of K^+ or Na^+ ions.[38] This substitution was further confirmed by the shift of the diffraction peaks to larger angles for both KNN-Al and KNN-Eu ceramics in comparison with pure KNN ceramic due to the lattice shrinkage, as shown in Figure 1b. The energy-dispersive X-ray (EDX) mappings of KNN-based ceramics are shown in Figure 1g-1l, Figure S1 and Figure S2. All elements were homogeneously distributed in KNN and KNN-Eu ceramics, while some Al-rich aggregates were observed for KNN-Al ceramics (see Figure S2e), possibly caused by minor impurities. The morphology of the KNN-based ceramics was characterized using SEM, as presented in Figure 1c-1d. Average grain sizes of 1.59 ± 0.03 μm, 1.49 ± 0.05 μm and 1.19 ± 0.03 μm were obtained for KNN, KNN-Al and KNN-Eu ceramics, respectively, indicating that the addition of Al^{3+} or Eu^{3+} can slightly inhibit the grain growth for KNN ceramic. Such phenomenon is also observed in other rare-earth ions doped KNN-based ceramics, such as Pr^{3+},Ho^{3+}, Er^{3+} and Sm^{3+}.[37, 39, 40]

The photochromic behavior of KNN, KNN-Al and KNN-Eu ceramics is presented in Figure 2. A reversible yellow-gray color change upon alternating 420 nm (0.12 W cm^{-2}) illumination and thermal treatment was observed for all ceramics, as shown in the insets in Figure 2a, 2b and 2c. Especially for KNN-Eu ceramics, the color change was more obvious in comparison with KNN and KNN-Al ceramics. Due to the photochromic effect, a significant decrease of reflectivity was obtained for all ceramics after illumination (see Figure 2a-2c). The maximum value of ΔR was larger upon incorporation of Al^{3+} or Eu^{3+}. Specifically, compared with KNN ceramics, the ΔR value was improved over the whole measured range when Eu^{3+}

ions were introduced, while for KNN-Al ceramic the Δ*R* value only a slight improvement was observed, on the short and long wavelength side, as Figure 2d shows. The maximum Δ*R* values obtained in KNN, KNN-Al and KNN-Eu were 21.8 %, 24.4 % and 39.2 %, respectively.

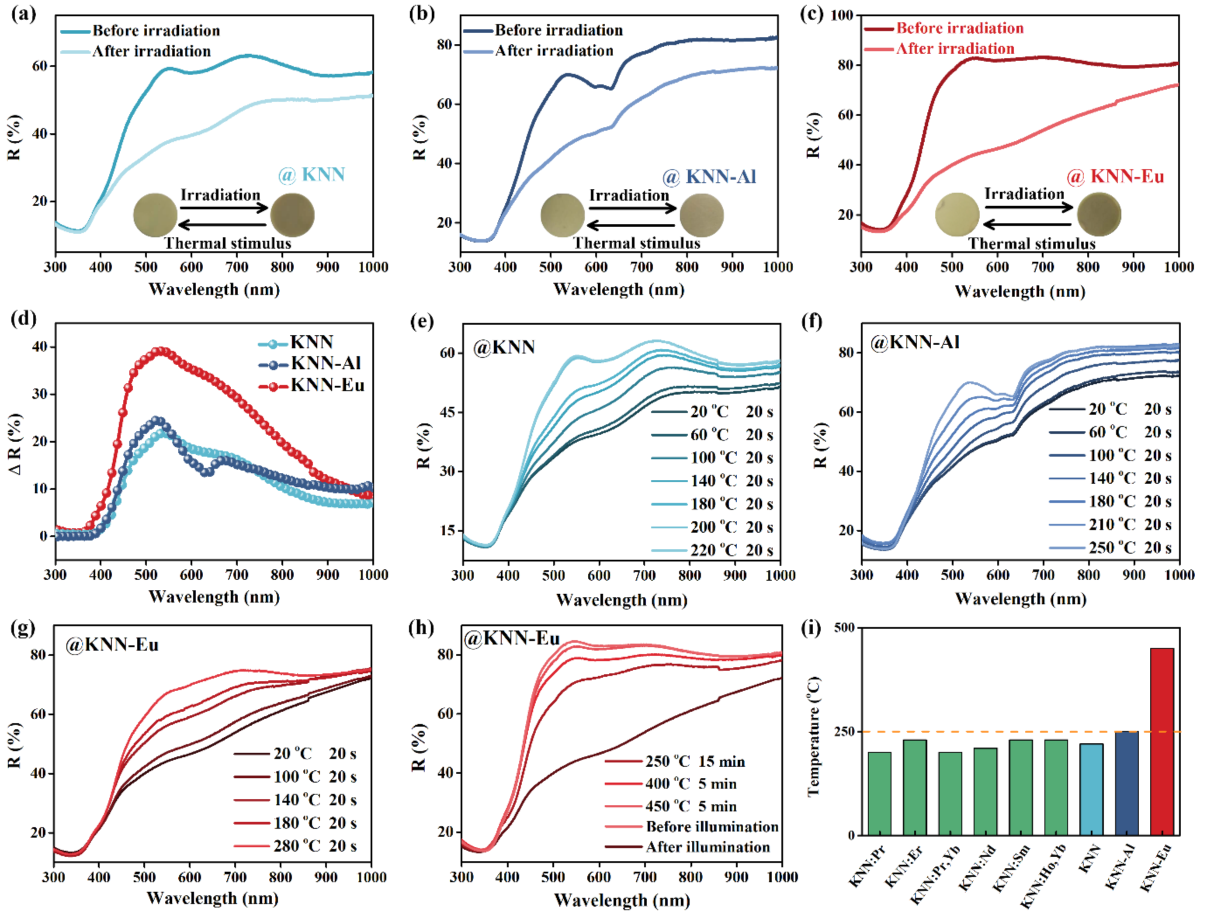

Figure 2. Reflectivity of a) KNN, b) KNN-Al and c) KNN-Eu ceramics before and after 420 nm illumination for 2 min. The inset shows the photograph of KNN, KNN-Al and KNN-Eu ceramics before and after illumination. d) A comparison of coloration contrast as a function of wavelength among KNN-based ceramics. Reflectivity of e) KNN, f) KNN-Al and g) KNN-Eu ceramics upon different thermal treatment temperatures for 20 s. h) Reflectivity of KNN-Eu ceramic upon different long-time thermal treatment temperatures. i) A comparison of required thermal treatment temperatures for completely bleaching of KNN-based ceramics doped with different rare earth ions.

To explain the high coloration contrast achieved in KNN-Eu ceramics, the bleaching processes of KNN, KNN-Al and KNN-Eu ceramics upon thermal treatment were studied. As Figure 2e-2g shows, the reflectivity gradually increases with the treatment temperature increases for all ceramics. A temperature of 200 ℃ and 250 ℃ for 20 s was sufficient to completely bleach the KNN and KNN-Al ceramics, respectively, while only part of the colored state was bleached for KNN-Eu ceramic upon thermal treatment at 280 ℃ for 20 s.

To investigate this improved thermal stability of KNN-Eu, the sample was subjected to thermal treatments at higher temperatures and for longer times. The results are displayed in Figure 2h. First, the sample was heated again to 250 °C but this time for 15 minutes to illustrate that increasing the duration of the thermal treatment at this temperature still does not allow to fully bleach the sample. Next, the sample was treated at higher temperatures during five minutes and the results show that the bleaching is only completed at a temperature of 450 °C. This thermal bleaching behavior is compared to other KNN-based ceramics in Figure 2i, and the corresponding detailed data can be found in Table S1. The treatment temperature of 450 ℃ for 5 min which is required for the KNN-Eu ceramic, is the highest bleaching temperature among ion-doped KNN ceramics, indicating that very deep-lying traps are formed in this case.[27, 36, 39, 41-45] Very shallow traps can be easily emptied by thermal energy available in ambient condition, while the release of deeper traps requires more thermal energy resulting in a higher bleaching temperature.[46, 47] It is well established that the photochromic behavior in robust oxides and ferroelectrics is related to cation vacancies or oxygen vacancies, generated during the high-temperature sintering or doping.[15, 26, 33, 48] Upon 420 nm illumination, the electrons located at the valence band or intermediate defects are excited to higher energy and some of them are captured by intrinsic defects such as oxygen vacancies, forming F-centers.[14, 26, 43] Subsequently, part of the incident light can be absorbed by the ceramic to release the electrons trapped by defects, changing the reflectivity and color of the ceramics. The electrons captured by the shallow traps are unstable and most of them are released at room temperature. In contrast, the electrons captured by the deep traps are more stable, which dominate the photochromic behavior. It has been confirmed in other research that enhanced photochromic behavior can be achieved through constructing deep traps.[19, 32] Therefore, the large coloration contrast obtained in KNN-Eu ceramics is attributed to the formation of deep traps via Eu^{3+} doping.

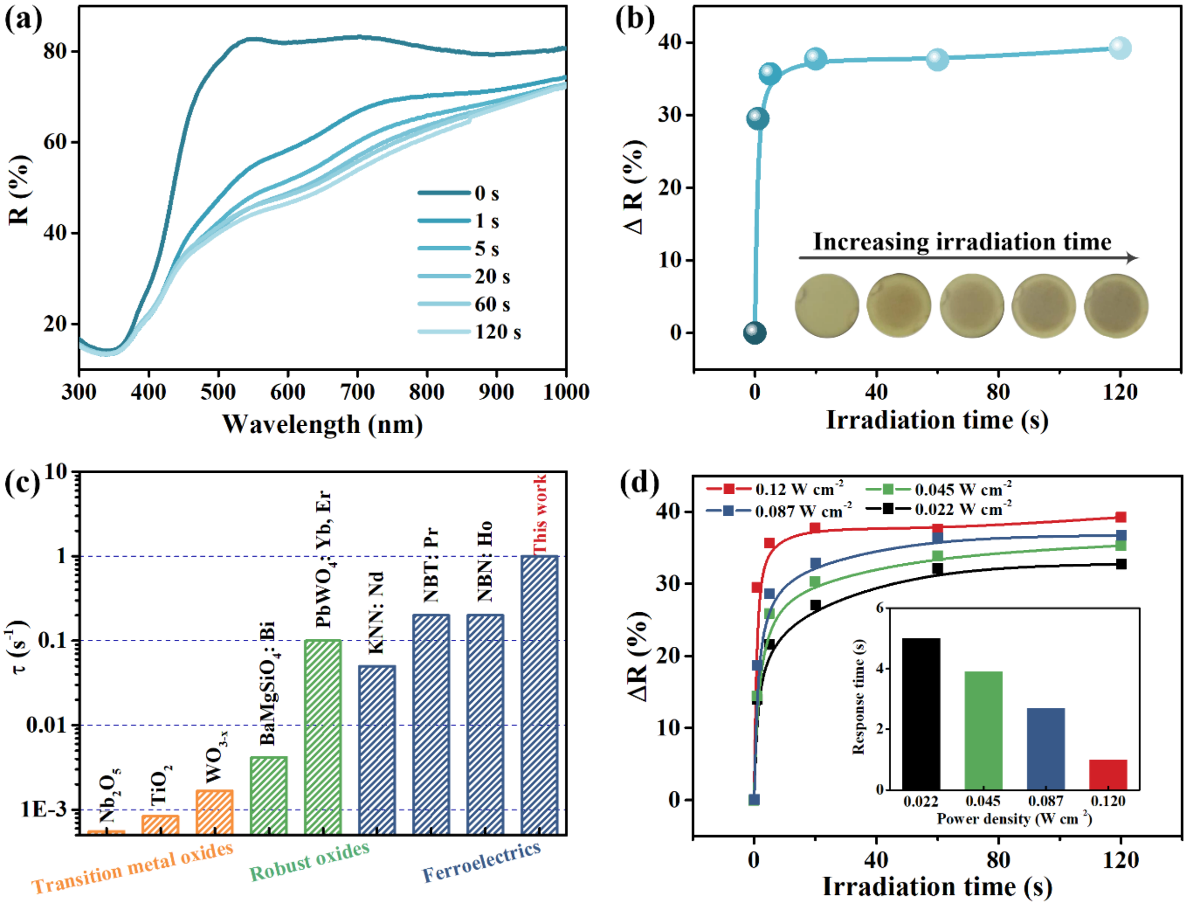

Figure 3. a) Reflectivity of KNN-Eu ceramic upon 420 nm light irradiation for different durations. b) Δ*R* value at 530 nm as a function of irradiation time with the corresponding photographs. c) Photo-response speed of some typical inorganic photochromic materials ($\tau = 1/t$, where t is the response time). d) Δ*R* value at 530 nm as a function of irradiation durations under different power densities with the intensity dependency of the response time.

Figure 3a presents the time-dependent reflectivity changes of KNN-Eu ceramic upon 420 nm illumination with a power density of 0.12 W cm^{-2}. As shown, the reflectivity drops quickly in the first seconds upon illumination and remains almost unchanged after 20 s of illumination.

Also, the color of the sample gradually turns gray with increasing irradiation time, which is consistent with the variation of Δ*R*, as shown in the inset in Figure 3b. The variation of Δ*R* at 530 nm as a function of irradiation time is shown in Figure 3b. It can be seen that KNN-Eu ceramic only requires about 1 s to attain 63 % of its maximum value, which is shorter than any other inorganic photochromic material (see Figure 3c). The detailed irradiation conditions of KNN-Eu and other typical inorganic photochromic materials are shown in Table 1.

Table 1. Response time of typical inorganic photochromic materials and the irradiation condition.

Materials	Response time (s)	Irradiation condition	Ref.
Nb_2O_5	1200	250 W high-pressure mercury lamp	[12]
TiO_2	900	365 nm, 0.003 W cm^{-2}	[11]
WO_{3-x}	600	UV lamp, 25 W	[56]
$BaMgSiO_4$: Bi	240	254 nm, 0.21 W cm^{-2}	[14]
$PbWO_4$:Yb, Er	10	532 nm, 0.6 W cm^{-2}	[25]
KNN: Nd	20	ultraviolet lamp 365 nm, 5 W	[27]
NBT: Pr	~5	laser diode, 407 nm, 200 mW	[23]
NBN: Ho	~5	laser diode 407 nm, 200 mW	[30]
KNN: Eu	~1	LED 420 nm, 0.12 W cm^{-2}	This work

It should be noted that the response time is related to the power density and wavelength of the light source. The response time of KNN-Eu, for example, increases to about 5 s when the illumination power is lowered from 0.12 W cm^{-2} to 0.022 W cm^{-2} (see Figure 3d and Figure S3). Hence, some minor improvements on the response time of other materials might be achieved by increasing the excitation power [25, 49] Also, a slight decrease of the maximum coloration contrast is observed upon the same illumination time of 120 s when the illumination power is lowered from 0.12 W cm^{-2} to 0.022 W cm^{-2}. For KNN-Eu ceramics, the penetration depth of the irradiating light inside the sample is limited due to its opacity. Upon illumination, the surface layer of the ceramic is quickly switched due to the high irradiation intensity, while the deeper layer needs a relatively long time to receive a sufficiently high photon flux to finish the photochromic behavior. Therefore, under the same illumination time, the coloration contrast achieved upon high power density illumination is larger than that upon low power density illumination. And the coloration contrast upon low power density illumination can be further improved through increasing the illumination time.

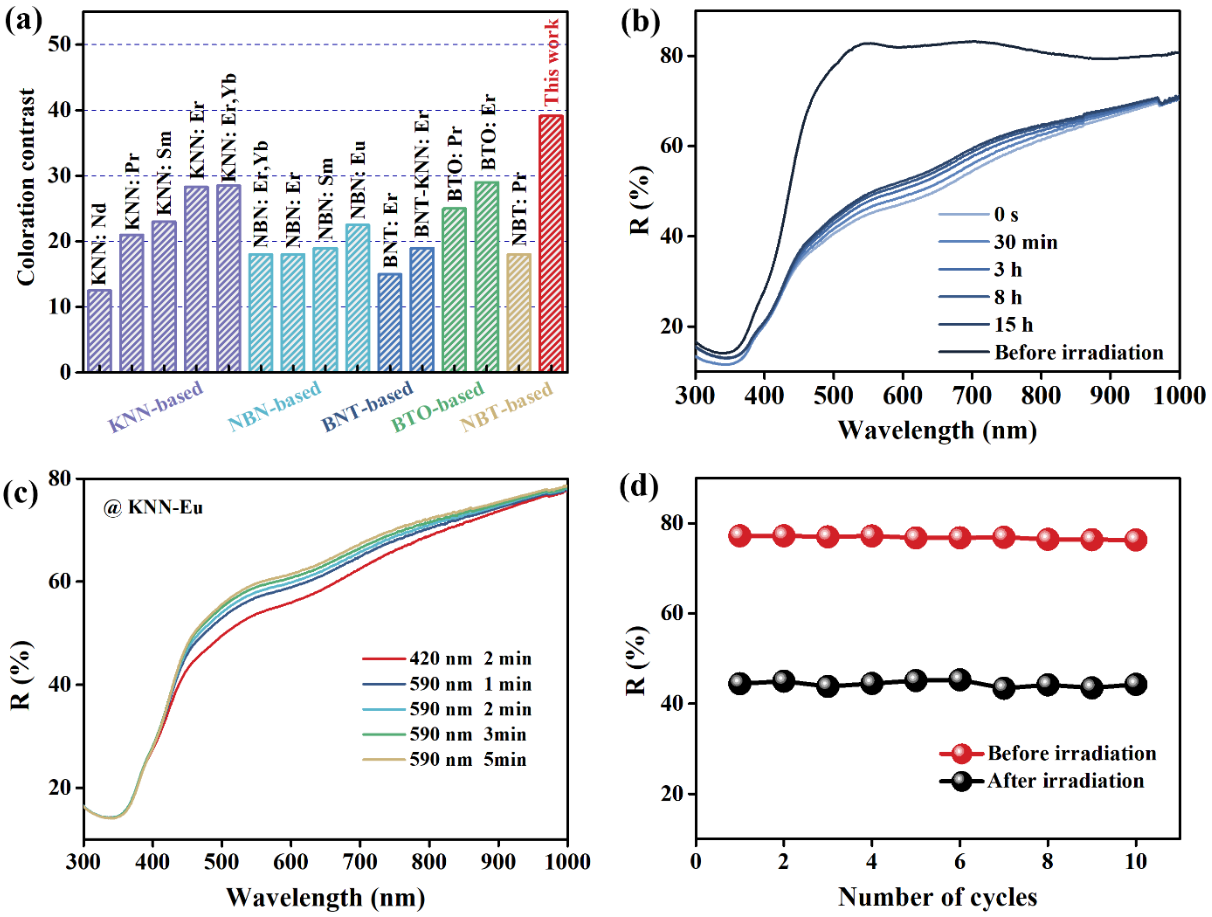

Figure 4. a) Maximum coloration contrast of KNN-Eu and other ferroelectric ceramics. b) Reflectivity of KNN-Eu ceramic before and after 420 nm irradiation recorded at different fading durations (0-15 h) in the dark. c) Reflectivity of KNN-Eu ceramics after 420 nm illumination for 2 min and then upon 590 nm illumination for different durations. d) Reflectivity at 530 nm upon alternative illumination (420 nm) and thermal stimulus (450 ℃) for 10 cycles.

Figure 4a presents a comparison of coloration contrast of KNN-Eu ceramic and other ferroelectric ceramics. Notably, KNN-Eu ceramic possesses the largest coloration contrast when compared with other ferroelectrics, the details of which are given in Table S2.[6, 23, 27, 28, 36, 42, 43, 50-55] The coloration contrast of ferroelectrics was enhanced from previously below 25 % to currently almost 40 %. Apart from fast response and strong coloration contrast, a stable colored state and good reversibility are also required for photochromic materials in practical applications. As Figure 4b shows, the reflectivity of the colored KNN-Eu ceramic increased slightly during the first 3-hour fading time and remained almost unchanged after fading for 8 h. Finally, a large ΔR value was maintained even after 15 h fading, indicating that the photogenerated colored state of KNN-Eu ceramics is stable at room temperature. Meanwhile, the colored state of KNN-Eu ceramics can only be partly bleached by low-energy photons and thermal treatment is required to achieve complete bleaching (see Figure 4c). A similar phenomenon is observed in KNN and KNN-Al ceramics (see Figure S4). Upon alternate illumination (420 nm) and thermal stimulus (450 °C), KNN-Eu ceramic shows a reversible yellow-gray color change. The reflectivity at 530 nm in both the colored and bleached state is almost unchanged after 10 cycles, as Figure 4d shows, exhibiting excellent reversibility. Therefore, fast photo-response, strong coloration contrast, excellent stability and good reversibility are all achieved in KNN-Eu ceramic, promising great potential in various real-time and high-reliability systems such as photo-switches and hand-writable information display.

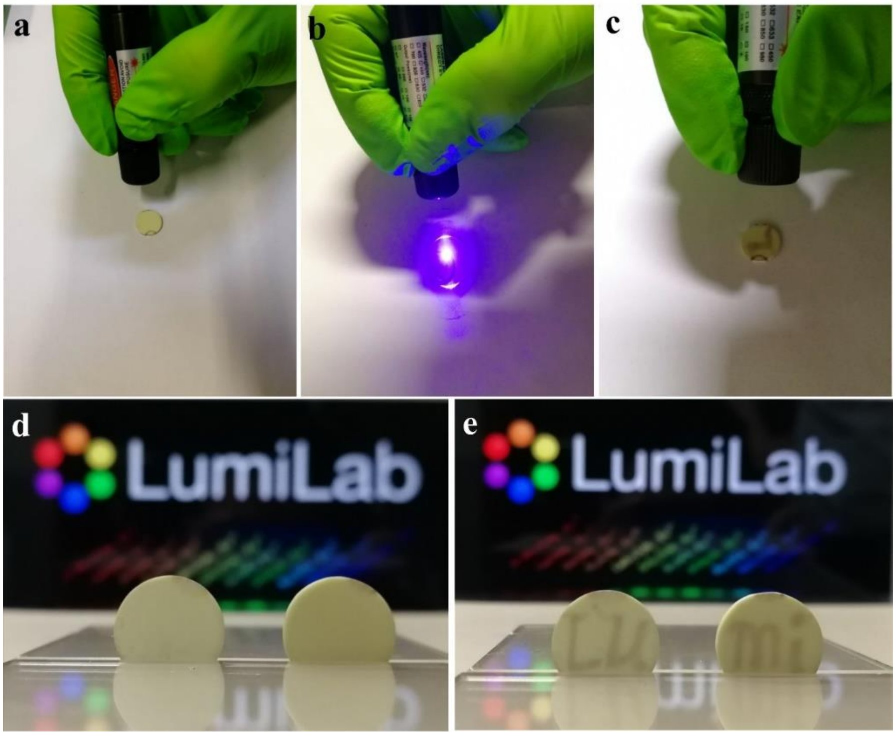

Figure 5. Hand-rewritable display with a laser pen recorded in KNN-Eu ceramic. a) before writing, b) during writing and c) after writing. d) Photograph of KNN-Eu ceramic before writing the characters of "Lumi". e) Photograph of KNN-Eu ceramic with the encoded characters of "Lumi".

As a proof of concept, a hand-rewritable information display with a portable laser-pen was demonstrated. The writing processes are shown in Figure 5a, b and c. Before writing, the ceramic was completely bleached via thermal treatment at 450 °C for 5 min (see Figure 5a). After that, a laser pen with a central wavelength of 405 nm (~0.15 W cm^{-2}) was employed to write the letter "L". Benefiting from the ultrafast photo-response and strong coloration contrast, a clear "L" was encoded in the KNN-Eu ceramic after instant handwriting, as shown in Figure 5c. Following similar processes, four letters of "Lumi" were recorded in two pieces of KNN-Eu ceramics, as displayed in Figure 5d and 5e. The four letters were clearly recorded in the ceramic, confirming its high resolution for hand-writing application. More interesting, the encoded letters can be totally erased after thermal stimulus and then the ceramic can be re-used for new data recording. A schematic diagram of KNN-Eu ceramics for information recording is shown in Figure S5. Although encoding patterns or characters has been achieved in photochromic materials, pre-patterned masks are usually required for these ceramics due to their long response time or low coloration contrast.[12, 14, 25] To the best of our knowledge, KNN-Eu ceramic is the first photochromic ceramic highly suitable for hand-rewritable and erasable information display.

3. Conclusion

A new strategy was proposed to achieve high photochromic performance via constructing deep-lying traps in ferroelectric ceramics. The obtained $K_{0.5}Na_{0.5}NbO_3$-Eu (KNN-Eu) ceramic shows a reversible yellow-gray color change upon alternate illumination (420 nm) and thermal stimulus (450 °C). The colored and initial states can be differentiated via one-second writing-in. To the best of our knowledge, a record reflectivity difference of 39.2 % is achieved between the colored and bleached ferroelectric ceramics. Benefiting from these excellent properties, real-time data recording with a portable laser pen was first realized in KNN-Eu ceramic to demonstrate instant and hand-writable information display. The results demonstrated in this work show an effective strategy to generate photochromic enhancement in ferroelectric ceramics. More importantly, it is expected to speed up the practical application of photochromic materials in numerous light-driven devices and a guidance to design other high-performance inorganic photochromic materials is provided.

4. Experimental Section

Sample preparation: $(K_{0.5}Na_{0.5})NbO_3$ (KNN), $(K_{0.5}Na_{0.5})NbO_3$-0.5 mol% Al^{3+} (KNN-Al) and $(K_{0.5}Na_{0.5})NbO_3$-0.5 mol% Eu^{3+} (KNN-Eu) were fabricated via a conventional solid-state reaction. K_2CO_3 (Sigma Aldrich, Saint Louis, MO, USA, 99.0 %), Na_2CO_3 (Alfa Aesar, Karlsruhe, Germany, 99.95 %), Nb_2O_5 (Alfa Aesar, Karlsruhe, Germany, 99.9 %), Al_2O_3 (Alfa Aesar, Karlsruhe, Germany, 99.99 %) and Eu_2O_3 (Alfa Aesar, Karlsruhe, Germany, 99.99 %) were adopted as raw materials. The precursors were first weighed according to each formula and then ball-milled with alcohol for 10 h. Then, the powders were calcined at 900 ℃ for 10 h, followed by 10-hour ball milling again. After drying, the obtained powders were mixed with 5 wt% polyvinyl alcohol (PVA) and then pressed uniaxially at ~200 MPa to produce pellets with a diameter of 13 mm and a thickness of 1.2 mm. The green pellets were first sintered at 650 ℃ for 2 h in air to remove the PVA and then sintered at 1130 ℃ for 2 h in air to obtain dense ceramics.

Sample characterization: Crystal structures of the fabricated ceramics were confirmed by powder XRD measurements using a Siemens D5000 diffractometer (40 kV, 40 mA) with Cu Kα1 radiation ($\lambda = 0.154$ nm), which were scanned from 20° to 80° in steps of 0.02° with 1.5 s integration time in each step. SEM was performed using a Hitachi S-3400N microscope, connected to a Thermo Scientific Noran 7 energy-dispersive X-ray (EDX) analysis system, under a pressure of 25 Pa and an accelerating voltage of 20 kV. The grain size was calculated using the software "Nano Measurer". The reflectivity spectra of the ceramic were recorded using a Perkin Elmer Lambda 1050 UV-Vis-NIR spectrophotometer equipped with a Spectralon-coated integrating sphere with PMT (photomultiplier) and InGaAs detectors. The photochromic switching experiments were performed using light emitting diode (LED) centered at 420 nm with a power density of 0.12 W cm^{-2}. The light bleaching processes were carried out using light emitting diode centered at 590 nm with a power of 1.5 W. For thermal bleaching, the ceramics were first irradiated with 420 nm light for 2 min to undergo a complete photochromic processes. Then the ceramics were subsequently treated at different temperatures (ranging from 20 ℃ to 280 ℃), and a 20-second treatment was carried out for each temperature. The thermal bleaching processes were carried out with a hot plate and a crucible. Before thermal stimulus, the crucible was first heated to the required temperature. Then, the sample was placed on the hot plate and kept for 20 s. After that, the sample was cooled to room temperature followed by the reflectivity measurement. The thermal stimulus of 250 ℃ for 15 min, 400 ℃ for 5 min and 450 ℃ for 5 min were carried out using a muffle furnace.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work is financially supported by the Ghent University's Special Research Fund. J. Du acknowledges BOF postdoctoral fellowship (No. BOF20/PDO/015). The authors acknowledge the financial support from FWO (project I002418N). D. Van der Heggen acknowledges the IOF of Ghent University for funding (F2020/IOF-ConcepTT/094).

Conflict of Interest

The authors declare no conflict of interest.

Received: ()
Revised: ()

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