A breakthrough in the intrinsic multiferroic temperature region in Prussian blue analogues†

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Thin films of [(FeII\textsuperscript{x}CrIII\textsuperscript{1-\textit{x}})]\textsubscript{1.5}[CrIII(CN)\textsubscript{6}]\textsubscript{1.77}H\textsubscript{2}O (0 < \textit{x} < 0.42) films at room-temperature were synthesized with an electrochemical method. Investigation on its ferroelectricity reveals that the origin of the SHG was attributed to the out-of-plane orientation of the electric-dipole moment induced by a distorted structure. Because SHG property is the prerequisite and necessary condition for ferroelectricity, it is expected that room-temperature ferroelectric in those high symmetrical crystal structures remains a great challenge.

In 2001, Ikeda et al. observed second-harmonic generation (SHG) signals from the Prussian blue analogues of [(FeII\textsuperscript{x}CrIII\textsuperscript{1-\textit{x}})]\textsubscript{1.5}[CrIII(CN)\textsubscript{6}]\textsubscript{1.77}H\textsubscript{2}O (0 < \textit{x} < 0.42) films at room-temperature. Investigation on its SHG property indicates that the origin of the SHG was attributed to the out-of-plane orientation of the electric-dipole moment induced by a distorted structure. Because SHG property is the prerequisite and necessary condition for ferroelectricity, it is expected that room-temperature ferroelectric may be obtained in this compound. Here we report the ferroelectric property of [(FeII\textsuperscript{x}CrIII\textsuperscript{1-\textit{x}})]\textsubscript{1.5}[CrIII(CN)\textsubscript{6}]\textsubscript{1.77}H\textsubscript{2}O (0 < \textit{x} < 0.42, y = 1.77) film. Investigation on its ferroelectricity reveals that the film displays spontaneous polarization in a very wide temperature range from 10 K to 310 K, for the first time realizing room-temperature ferroelectric in the Prussian blue analogues.

**Introduction**

Multiferroics generally are materials with two or three ferroic orders (magnetic, ferroelectric, or ferroelastic) coexisting in the same phase. Because magnetoelastic coupling effects (including in magnetodielectrics and magnetocapacitance) may occur in these materials, multiferroics have broad applications in memory storage devices, optoelectronic devices, and ferroelectrics. Electric order temperature in the former occurs at low temperature (77–160 K), while the electric order occurring at room-temperature in the latter is from the PVDF, instead of Prussian blue analogues themselves. Therefore, how to realize the room-temperature ferroelectric in those high symmetrical crystal structures remains a great challenge.

In 2001, Ikeda et al. observed second-harmonic generation (SHG) signals from the Prussian blue analogues of [(FeII\textsuperscript{x}CrIII\textsuperscript{1-\textit{x}})]\textsubscript{1.5}[CrIII(CN)\textsubscript{6}]\textsubscript{1.77}H\textsubscript{2}O (0 < \textit{x} < 0.42) films at room-temperature. Investigation on its SHG property indicates that the origin of the SHG was attributed to the out-of-plane orientation of the electric-dipole moment induced by a distorted structure. Because SHG property is the prerequisite and necessary condition for ferroelectricity, it is expected that room-temperature ferroelectric may be obtained in this compound. Here we report the ferroelectric property of [(FeII\textsuperscript{x}CrIII\textsuperscript{1-\textit{x}})]\textsubscript{1.5}[CrIII(CN)\textsubscript{6}]\textsubscript{1.77}H\textsubscript{2}O (0 < \textit{x} < 0.42, y = 1.77) film. Investigation on its ferroelectricity reveals that the film displays spontaneous polarization in a very wide temperature range from 10 K to 310 K, for the first time realizing room-temperature ferroelectric in the Prussian blue analogues.

**Experiment details**

**Sample preparation**

All reagents used for the synthesis of film were reagent grade and without further purification. The thin film 1 was synthesized in an electrochemical method reported previously. Electronically reducing experiments were carried out on CHI600E electrochemical workstation with fluorine-doped tin oxide (FTO)-coated glass slides as working electrode. The saturated calomel electrode (SCE) and platinum plate were used as reference electrode and auxiliary electrode, respectively.
electrolyte solutions were prepared by dissolving K₃Cr(CN)₆ (0.1 mmol), CrCl₃•6H₂O (0.1 mmol), and anhydrous FeCl₃ (0.05 mmol) in 20 mL deionized water. The bulk electrolysis was carried out at −0.84 V vs. SCE. The thickness of film 1 was controlled by the reaction time. Typically, 3 μm thickness film 1 suitable for the ferroelectric measurement was obtained when the reduction reaction time is about 2000 seconds (Fig. S1†).

**Powder X-ray diffraction**

Powder X-ray diffraction (PXRD) patterns of the film 1 and crushed film 1 were recorded on a Rigaku Ultima IV diffractometer with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator at a scanning rate of 10° min⁻¹ from 10° to 60°.

**Ferroelectricity**

The polarization–electric field (P–E) hysteresis loops were measured with a RADIANT Precision Premier II analyzer using the positive up negative down (PUND) method in order to eliminate the small electric conductivity contributions. The temperature was controlled by Janis cryogenic refrigeration system between 10 K and 310 K under vacuum. The piezoresponse force microscopy (PFM) measurement was performed on a commercial piezoresponse microscope (Cypher, Asylum Research) by using the conductive Pt/Ir-coated silicon probes (EFM-20, Nanoworld).

**Thermal properties**

Differential scanning calorimeter (DSC) measurement was performed on a NETZSCH DSC 200F3 instrument. Thermogrammic analysis (TGA) was measured using an SDT-Q600 thermal analyzer at a heating rate of 10 K min⁻¹ in nitrogen.

**Optical second harmonic generation experiments**

The signal of second-harmonic generation (SHG) was performed by using Q-switched Nd:YAG laser (1064 nm) with an incidence angle of about 35° onto the film 1 and crushed film 1.

**X-ray absorption spectroscopy**

The X-ray absorption spectra (XAS) were recorded at the XAS station (BL14W1) of the Shanghai Synchrotron Radiation Facility (SSRF). The electron storage ring was operated at 3.5 GeV. Si (111) double-crystal was used as the monochromator, and the data was collected with transition mode under ambient conditions. The X-ray absorption of Fe foil and Cr foil at K-edge were measured at different temperatures. The X-ray absorption of Fe foil and Cr foil at K-edge were measured using a RADIANT Precision Premier II analyzer using the positive up negative down (PUND) method in order to eliminate the small electric conductivity contributions. The temperature was controlled by Janis cryogenic refrigeration system between 10 K and 310 K under vacuum. The piezoresponse force microscopy (PFM) measurement was performed on a commercial piezoresponse microscope (Cypher, Asylum Research) by using the conductive Pt/Ir-coated silicon probes (EFM-20, Nanoworld).

**Dielectric measurements**

The dielectric permittivity ε (ε = εʹ − iε″) was measured using the two-probe ac impedance method in the testing temperature range from 10 to 310 K and the frequency at 10 kHz on Wayne Kerr 6500B analyzer.

**Magnetic measurement**

Temperature dependent magnetic susceptibility was measured by Quantum Design MPMS Superconducting Quantum Interference Device (SQUID) XL-7.

**Results and discussion**

Owing to the deviation between feeding ratio and actual ratio of reaction solution related to the hydrolysis and oxidation of transition metal ions during electrochemically reducing process, the composition of the film 1 was determined by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) (Table S1†) so as to obtain more accurate measurement results. The ICP-MS study on the film 1 indicates that its mole ratio of Fe to Ni is between 1 : 3.825 and 1 : 4.436, and hence the film 1 formulated as [(FeII/CrIII(CN)6)]x yH₂O (x = 0.30–0.35, y = 1.77) (1), consistent with TGA result (Fig. S2a†). Based on the PXRD patterns of the film 1 on the FTO substrate (here and after namely, film 1) (Fig. S3†), which show the highest peak oriented in the (110) direction, it is reasonable to conclude that the film 1 on the FTO substrate crystallized in C2 space group. For comparison, the PXRD patterns of the crushed film 1 stripped from the FTO substrate (here and after namely, crushed film 1) was also investigated respectively. It exhibited highest peak oriented in the (200) direction, indicating that they crystallized in F23 space group. Consistent with previous results, the film 1 displays the SHG property, while the crushed film 1 does not (Fig. S4†).

The ferroelectricity was characterized by measuring the polarization–electric field (P–E) hysteresis loop. At room temperature (Fig. 1c), it exhibited typical hysteresis loop, confirming that film 1 is a ferroelectric. The remnant polarization...
The ferroelectricity of film 1 was also investigated by measuring its domain on the surface by using the PFM measurements. Fig. 2a and b illustrated the images obtained from the out-of-plane PFM phase and amplitude mapping overlaid on three dimensional (3D) topography, respectively. The PFM phase mapping reveals the irregular shape domain structure of film 1, and the neighboring domains have about 180° phase contrast. The film of 1 is composed of many about 1 μm size crystallites (Fig. 2a and S1b†), and there were no obvious correlation between ferroelectric domain and local morphology of film surface. To further confirm the ferroelectricity in film 1, local PFM-based hysteresis loop measurement were carried out under the resonance-enhanced PFM mode. As shown in Fig. 2c and d, the characteristic hysteresis (180° reversal of phase signal) and butterfly loops were observed distinctly. These results, together with no significant change observed in the hysteresis under different applied voltages (Fig. S6†), indicate that the ferroelectricity in film 1 is its inherent property.26–29

Because both the film 1 and the crushed film 1 have the same vacancy, the X-ray absorption (XAS) of the crushed film 1 was performed (Fig. S7–S9†) so as to obtain more accurate coordination environment around the vacancy. As shown in Fig. 3a, the peak at about 1.5 Å (uncorrected, coordination element difference would cause the peak variation in R space), attributed to the coordination number of the Cr–C/N in the crushed film 1 (4.7 ± 1.0) is close to that in the K₃Cr(CN)₆ (4.9 ± 1.3), demonstrating that the coordination number of the Cr–C/N in the crushed film 1 is unchanged (Table S2†).

In order to disclose the ferroelectric origin, the structure of film 1 and crushed film 1 were respectively simulated by using the Materials Studio software.21 Owing to the vacancy sites usually occupied by the coordinated water and solvent water molecules, it is reasonable to deduce existence of CN–Fe/OH₂ site in the crushed film 1. Thus, that the film 1 exhibits ferroelectricity while the crushed film 1 does not is understandable.
As shown in Fig. 4a and b, although random vacancies of [Cr\textsuperscript{III}(CN)\textsubscript{6}]\textsuperscript{3–} in the crushed film 1 will lead to the generation of the dipole moment in the CN-Cr\textsuperscript{II}/Fe\textsuperscript{II}–OH\textsubscript{2}, owing to F23 space group having twelve symmetric elements (E, B\textsubscript{C}1, 3C\textsubscript{2}) which leads to the distance in each Cr\textsuperscript{III}–Cr\textsuperscript{III}/Fe\textsuperscript{II} in the crushed film 1 being exactly the same (5.250 Å) and the angle of Cr\textsuperscript{II}/Cr\textsuperscript{II}–Cr\textsuperscript{III} and Cr\textsuperscript{II}/Fe\textsuperscript{II}–Cr\textsuperscript{III}–Fe\textsuperscript{II} being 90°, the total dipole moment of the CN-Cr\textsuperscript{II}/Fe\textsuperscript{II}–OH\textsubscript{2} around vacancies of [Cr\textsuperscript{III}(CN)\textsubscript{6}]\textsuperscript{3–} canceled out each other. In comparison, owing to the C2 space group only having two (E, C\textsubscript{2}) not only the distances of adjacent Cr\textsuperscript{III}–Cr\textsuperscript{III}/Fe\textsuperscript{II} are different, but also the angles of Cr\textsuperscript{III}–Cr\textsuperscript{III}/Fe\textsuperscript{II}–Cr\textsuperscript{III} and Cr\textsuperscript{II}/Fe\textsuperscript{II}–Cr\textsuperscript{III}–Cr\textsuperscript{II}/Fe\textsuperscript{II} are deviated from 90°. As a result, the total dipole moment of the CN–Cr\textsuperscript{III}/Fe\textsuperscript{II}–OH\textsubscript{2} around vacancies of [Cr\textsuperscript{III}(CN)\textsubscript{6}]\textsuperscript{3–} can not cancel out.

Fig. 5a shows the thermal variation of χ\textsubscript{m} measured for the crushed film 1 at 10 Oe and temperature-dependent dielectric constant of the film 1 at f = 10 kHz, respectively. With the increase of the temperature, the value of χ\textsubscript{m} gradually increased from 0.0052 cm\textsuperscript{3} mol\textsuperscript{–1} at 300 K to a maximum of 124.23 cm\textsuperscript{3} mol\textsuperscript{–1} at 2 K. The value of χ\textsubscript{m} increases sharply at about 210 K, indicating a transition from paramagnetic state to a ferromagnetic state. Consistently, the zero-field cooled (ZFC) and the field-cooled (FC) magnetization of the crushed film 1 at 10 Oe exhibits a typical bifurcation at 210 K (Fig. S10†), further confirming the transition from a paramagnetic state to a ferromagnetic state around 210 K. The magnetic property of the crushed film 1 is basically consistent with that observed in the Prussian blue analogues of (Fe\textsuperscript{II}–Cr\textsuperscript{III}/Fe\textsuperscript{II}–Cr\textsuperscript{III}), which indicates the potential coupling between magnetization and electric polarization.\textsuperscript{37} One of the possible reasons is that the magnetoelectric coupling effect in the film 1 is too weak.

Conclusions

In conclusion, the room temperature ferroelectricity of film 1 was realized through inducing vacancy defects and interactions between the film and FTO substrate. Investigation on the ferroelectricity of the film 1 reveals that it exhibits ferroelectric in the temperature range from 10 K to 310 K. Study on the X-ray absorption (XAS) of the crushed film 1 and the simulation of the structure of film 1 and crushed film 1 by using the Materials Studio software indicate that the vacancy defects in the film 1 and interactions between the film 1 and FTO substrate play a key contribution to its ferroelectricity of the film 1. Considering the fact that the magnetic phase transition point is up to 210 K, the film 1 is a multiferroic material and its magneto/electric coexistence can be as high as 210 K. Thus present work not only open a way to the preparation of the ferroelectric materials, but also lay a solid foundation for the application of Prussian blue magneto/electric coexistence materials, when considered that fact that some of Prussian blue analogues exhibit a high magnetic order temperature.

Conflicts of interest

There are no conflicts to declare.

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