Study on the Difference of Photochromic and Thermochromic Mechanism of Ethylenediamine Trimolybdate

Dehui Sun,[1,2] Hongjie Zhang,*[1] Cheng Wang,[1] Jilin Zhang,[1] Jiangbo Yu,[1] and Chunyun Peng[1,2]
[1]*Key Lab of Rare Earth Chemistry and Physics, Chinese Academy of Sciences, Changchun 130022, P. R. China*
[2]*Graduate School of the Chinese Academy of Science, Beijing 100049, P. R. China*

(Received July 6, 2006; CL-060769; E-mail: hongjie@ciac.jl.cn)

Ethylenediamine trimolybdate (($C_2H_{10}N_2$)[Mo_3O_{10}], denoted as ENTMo) shows unusual photochromic and thermochromic properties. The color of the white ENTMo compounds becomes reddish brown gradually under UV irradiation, and changes gradually to blue-black upon annealing. XRD patterns and FT-IR spectra verify that the crystal structure of the colored samples is almost unchanged except distortion. UV–vis diffuse reflectance spectra (DRS) and ESR spectra of the photochromic and the thermochromic samples could confirm that there must exist difference between thermochromic and photochromic mechanism.

One of the most important properties of alkylammonium polyoxometalates, under irradiation or annealing, is the capability to accept one electron to give rise to mixed-valence state species of metal ions.[1–5] The mixed-valence state species of metal ions are close related to the photochromism or thermochromism of alkylammonium polyoxometalates. Yamase[5] studied photochromic properties of the single crystal alkylammonium polyoxomolybdates and proposed a photochromic mechanism. This proposed mechanism is widely accepted in this field.[6–9] It is well known that the chromic mechanism of alkylammonium polyoxometalates mainly depends on two aspects: reduced mechanism from Mo^{VI} to Mo^{V} and optical transition mechanism of d^1 electrons. The former can be characterized by ESR and XPS, while the latter can be presented by absorption spectrum or UV–vis diffuse reflectance spectra (DRS). In this work, we have found that the ENTMo compounds synthesized by hydrothermal reaction show unusual photochromism and thermochromism. The DRS and the ESR of the irradiated and the annealed samples are obviously different. Although the thermochromism mechanism of ENTMo is still unclear, it could be concluded that the difference between the irradiated and the annealed samples mainly results from the difference of chromic mechanism.

ENTMo with needle-like crystal particles was prepared according to reported procedures.[10] The ENTMo was subjected to milling using an agate mortar to offer small polycrystalline powder suitable for photochromic and thermochromic experiments. The photochromic experiments were carried out using a 500-W high-pressure mercury lamp as the light source at 15 °C. The distance between the lamp and the sample was 8 cm. The samples were irradiated for different time between 0 and 150 min in air, respectively. The thermochromic experiments were performed at different temperature ranging from 20 to 250 °C for 60 min in a conventional furnace under atmospheric pressure because the samples are very stable below 270 °C.

Fourier transform infrared (FT-IR) absorption spectra were recorded in the range of 4000–400 cm^{-1} on a model FTS135 infrared spectrophotometer operated at a resolution of 1 cm^{-1}. X-ray diffraction (XRD) was carried out on a D/Max 2500 V/PC X-ray diffractometer using high-intensity Cu Kα1 radiation ($\lambda = 1.54056$ Å). The X-ray photoelectron spectra (XPS) were obtained on a VG ESCALAB MK II photoelectron spectroscope using monochromatic Mg Kα (1253.6 eV) radiation. The electron spin resonance (ESR) spectra of the colored samples were recorded on a JESFE-3AX spectrometer at 77 K. UV–vis diffuse reflectance spectra (DRS) measurements were performed on a HITACHI U-4100 spectrophotometer.

FT-IR spectra verify that the molecular framework of all the colored samples remains almost unchanged. XRD patterns show that the crystal structure of the colored samples remains almost unchanged except slight structure distortion during irradiation or annealing process. The XPS results show that the Mo^{VI} are partly reduced to Mo^{V} in all the colored samples, with the binding energy being 232.5 and 235.7 eV for Mo^{VI}, 231.4 and 234.6 eV for Mo^{V}.[11]

The ESR spectra in Figure 1 exhibit different characteristic ESR signals for the irradiated and the annealed samples. For the photochromic samples (Figure 1a), they contain two sets of ESR signals, a triplet strong ESR signals (1:2:1) at $g_1 = 1.955$, $g_2 = 1.915$, $g_3 = 1.873$ and a very weak sextet signals. The first set of ESR signals is attributed to the superhyperfine interaction

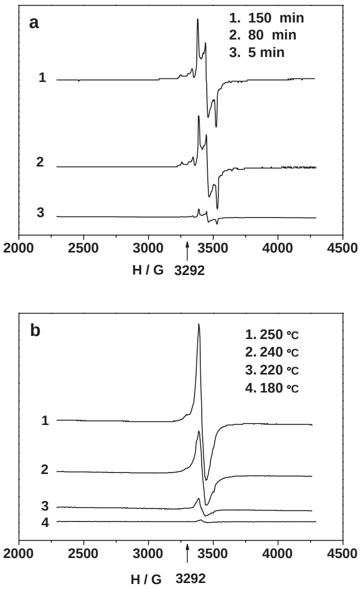

Figure 1. ESR spectra of (a) the irradiated sample for various irradiation time and (b) the annealed sample at various annealing temperature for 60 min.

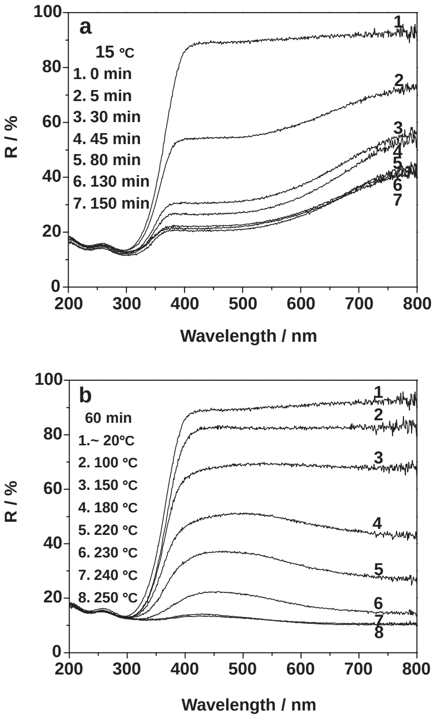

Figure 2. UV–vis DRS of the samples treated under different conditions, (a) irradiation with 365 nm UV light for different time at 15 °C in air, (b) annealing at different temperature for 60 min.

of the unpaired electron of Mo^V with a ^1H nucleus ($I = 1/2$). The nature of the middle intense ESR signal originates from $^{96}Mo^V$ ($I = 0$). The second set of ESR signals is assigned to the hyperfine interaction of the unpaired electron of Mo^V with ^{95}Mo (15.7%) and ^{97}Mo (9.5%) molybdenum isotopes. The hyperfine structure at 77 K and room temperature (no ESR) implies that the electron could be localized one molybdenum atom in the ESR time scale.[1] For the thermochromic samples (Figure 1b), they also exhibit three signals with principal g values 1.953, 1.922, and 1.873, but the anisotropic hyperfine structure becomes obscure. The faint hyperfine structure at 77 K implies that the electron could be delocalized at this temperature to some extent.[1] The difference of the content of Mo^V is not responsible for the difference of the ESR signals of the irradiated and the annealed samples because the characteristic of respective ESR signals is almost identical for the high or the low content of Mo^V. It is obvious that the difference results from the difference of the reduced mechanism.

UV–vis DRS of the treated samples under different conditions are shown in Figure 2. From these spectra, similar absorption behavior can be observed below 400 nm. There are two absorption bands in the range of 200–400 nm, which are centered at 235 and 300 nm, respectively. The strong absorption bands are assigned to intrinsic absorption bands of the compound, that is, a transition from its valence band to its conduction band although there still remain elusive from literature.[5] In visible region, the maximal wavelength is ca. 500 nm after photoirradiation while is ca. 700 nm after annealing. The optical absorption for the colored ENTMo compounds can be attributed to Mo^V–O–Mo^{VI} → Mo^{VI}–O–Mo^V intervalence charge transfer (IVCT) and/or d–d transition of Mo^V ($4d^1$).[5] However, it can be seen from Figures 2a and 2b, the colors for the samples treated by irradiation and annealing processes are different. The white samples always change to reddish brown under irradiation and blue-black after annealing. The color difference shows that there could be different Mo^V sites for the irradiated and the annealed samples. The different Mo^V sites can result in the difference of $4d^1$ in crystal field circumstance and delocalization extent,[5] thus influence d–d transition and IVCT. Although the reason resulting in the difference of the absorption bands in visible region for the photochromic and the thermochromic samples is still unclear, it is identifiable that there must exist some differences in the transition of electrons.

Therefore, it could be concluded that the difference of chromic mechanisms for the photochromic and the thermochromic samples results in the difference of the DRS in visible region and the ESR.

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