Large and reversible in-situ up-conversion photoluminescence modulation based on photochromism via electric-field and thermal stimulus in ferroelectrics

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ABSTRACT

A large and reversible up-conversion (UC) photoluminescence modulation via both thermal and electric-field stimulus based on the photochromic reactions has been developed in a novel material: Er3+/Yb3+ co-doped K0.5Na0.5NbO3 ferroelectrics. After visible light irradiation, the ceramics exhibit a significant photochromism phenomenon turning from pale yellow to gray. The gray color can be eliminated via heat treatment or partly removed by an electric field stimulation. Upon 390-nm light irradiation for 4 min and thermal treatment at 200 °C for 5 min, the ceramics show a large modulation ratio (96%). In addition, the UC photoluminescence modulation can be in-situ operated by alternating the light irradiation and electric-field, showing an enhancing factor of 120% for the 390-nm light irradiated ceramics via applying an electric-field stimulation (12.5 kV/cm, 1 min). The developed ferroelectrics with large and reversible photoluminescence modulation through thermal stimulus and electric-field have great potential for digital memory and optoelectronic device applications.

1. Introduction

Photochromic (PC) luminescence emission modulation materials, which possess both PC and emission modulation behaviors in one single material, have aroused great interest because of their potential applications in optical information memories, optical switches and bioimaging [1–5]. Photochromism is usually termed as a reversible color change phenomenon via alternating visible light irradiation and another stimulus such as heat, and ultraviolet light [6]. And with PC reactions, the luminescence emission intensity can be modulated through the energy transfer between the color center and activators [7]. For applications in optical switches or memories, the decreased and increased luminescence emissions represent “off” and “on” or “0” and “1” code, respectively. Importantly, optical digital memories can be written/erased via a coloration/decoloration process with easiness utilizing PC luminescence emission modulation materials [3,4]. Enormous researches have been conducted to study organic materials with the performance of PC luminescence emission modulation, such as diarylethenes, fulgides and spiropyrans [8–10]. Yet few researches have been carried out on investigating luminescence emission modulation in inorganic materials based on PC reactions. In contrast to organic materials, the inorganic ones have exceptional advantages in heat endurance, fatigue resistance, and mechanical strength [11,12]. Some inorganic materials (V2O5, WO3, MoO3, TiO2, etc.) have been demonstrated to have PC behavior. However, the reversibility of these materials is poor [13–16]. More importantly, no emission modulation property has been reported for them.

Lately, another material system, rare-earth element doped ferroelectrics including K0.5Na0.5NbO3 (KNN), Na0.5Bi4.5Ti4O15 (NBT) and Na0.5Bi2.5Nb2O9 (NBN), has been found to possess a reversible PC behavior. However, the reversibility of these materials is poor [16,17,18]. More importantly, no emission modulation property has been reported for them.

As we know, ferroelectrics have been applied in nonvolatile random access memories based on the ferroelectric domain switching [21,22]. One can expect that the memory density can be highly increased in ferroelectric materials by combining these two memory mechanisms, namely, domain switching and PC reaction. The piezoelectricity and ferroelectricity of KNN ceramics are much superior to those of NBN and NBT [23]. Whereas the reported PC photoluminescence modulation ratio of KNN ceramics is relative low (< 80%) [17,18]. In addition, as reported in all ferroelectrics, the reversible modulation process is realized through alternating light irradiation and thermal stimulus Δ (light-heat). The thermal treatment Δ is carried out on a heater and the materials must be cooled down before photoluminescence measurement, greatly limiting their practical applications [7,17–20]. Therefore, developing other feasible method for photoluminescence modulation is of great importance. The electric field (E-field) can be conveniently applied or...
removed, while the thermal treatment needs a heat transfer and a cooling process. Obviously, E-field stimulus is easier to be controlled and responds much faster than the thermal stimulation during photoluminescence modulation. To the authors’ knowledge, photoluminescence modulation is not reported via applying an E-field upon the PC materials. Delightedly, large and reversible in-situ photoluminescence modulation has been achieved in Er\(^{3+}/\)Yb\(^{3+}\) co-doped K\(_{0.5}\)Na\(_{0.5}\)NbO\(_3\) ferroelectrics through alternating light irradiation and E-field stimulus (light-E-field) besides the light-heat method.

Herein, a novel PC ferroelectric material of Er\(^{3+}/\)Yb\(^{3+}\) co-doped K\(_{0.5}\)Na\(_{0.5}\)NbO\(_3\) with large and excellent reversible UC photoluminescence modulation is reported. Alternating light irradiation and heat treatment or E-field stimulation, the ceramics can be colored and decolored converting between gray and pale yellow. Meanwhile with the PC reactions, the luminescent emission at 551 nm is effectively modulated. Moreover, the mechanism of light-heat and light-E-field photoluminescence modulation upon PC is explained.

2. Experimental

2.1. Material fabrication

(K\(_{0.5}\)Na\(_{0.5}\))\(_{0.998-x}\)Er\(_{0.002+y}\)Yb\(_x\)NbO\(_3\) (x = 0, 0.002, 0.004, 0.006, 0.008) ceramics, abbreviated as KNEN\(_x\)Yb, were fabricated by a conventional solid-state reaction method. High-purity K\(_2\)CO\(_3\) (99.5%), Na\(_2\)CO\(_3\) (99.8%), Nb\(_2\)O\(_5\) (99.5%), Er\(_2\)O\(_3\) (99.9%), Yb\(_2\)O\(_3\) (99.9%) powders were used as raw materials. These powders were weighted in the stoichiometric ratio and ball-milled with alcohol before calcining at 850 °C for 4 h in air. The calcined powders were re-ball-milled in alcohol and mixed with 5 wt % poly (vinyl alcohol) (PVA) solution thoroughly after drying. The mixture was pressed into disk-shaped pellets and finally sintered at 1110–1220 °C for 4 h in atmosphere. The ceramics were ground to a thickness of 400 μm. Then silver electrodes were coated on one side of samples, and semitransparent Au electrodes were deposited on the other side by ion sputtering for ferroelectric hysteresis loop and in-situ light-E-field photoluminescence modulation measurements. The semitransparent electrode enables the irradiation, excitation and emission light to pass through it during the in-situ light-E-field photoluminescence modulation measurements.