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Photoluminescence critical behavior in Er^{3+} doped $Ba_{0.77}Ca_{0.23}TiO_3$ ceramic

Zhang Liang [a], Enwei Sun [a], Shenghai Pei [a], Jingyang Zhang [a], Feng Qin [a], Yangdong Zheng [b], Hua Zhao [c], Zhiguo Zhang [a, d, *], Wenwu Cao [a, d, e, **]

[a] Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150080, China
[b] Department of Physics, Harbin Institute of Technology, Harbin 150001, China
[c] School of Materials and Engineering, Harbin Institute of Technology, Harbin 150001, China
[d] Laboratory of Sono- and Photo- Theranostic Technologies, Harbin Institute of Technology, Harbin 150080, China
[e] Department of Mathematics and Materials Research Institute, The Pennsylvania State University, State College, 16802, USA

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ABSTRACT

We developed a non-contact and non-destructive method to detect Curie point (T_C) in Er^{3+} doped $Ba_{0.77}Ca_{0.23}TiO_3$ (BCT) ferroelectric ceramic. Through investigating the photoluminescence (PL) spectra of Er^{3+} doped BCT ceramic we found that PL characteristics in ferroelectrics demonstrates critical behavior around T_C. Both intensity and peak positions of the Stark sub-peaks originating from $^4S_{3/2}$ to $^4I_{15/2}$ transition change dramatically, and can be fitted with two different lines below and above T_C. The inflection points of the PL characteristics are at the same temperature of 381(1) K, and coincident with the T_C (381 K) determined by the dielectric temperature spectrum.

1. Introduction

Ferroelectrics are widely used for medical, industrial, and military applications [1,2]. One of their unique characteristics, the critical behavior, has been extensively studied because it is a key factor for the application of ferroelectrics. Around the Curie point (T_C) many ferroelectric characteristics change dramatically, including dielectricity, piezoelectricity, and ferroelectricity [3–6]. Recently, researchers have doped ferroelectrics with rare earth ions, which have abundant energy levels for photoluminescence (PL). They then examined the PL characteristics of these special hosts [7–10]. To date, this area of research has focused on the electrical-mechanical-optical coupling for multifunctional materials [11–13]. Ranjan et al., describe these materials as "luminescent ferroelectric/piezoelectric" [14]. As the PL of rare earth (RE) ions is quite sensitive to crystal field symmetry, it is natural to wonder how the PL will act around T_C. Will it also exhibit critical behavior? This knowledge will provide a new way to detect the Curie point of ferroelectrics. PL measurement has an advantage over the standard dielectric temperature spectra method, because PL monitoring is a non-contact and non-destructive measurement that does not require electrodes. Compared with other non-contact measurements, such as XRD analysis or Raman spectrum analysis, the equipment for PL measurements is much cheaper and available in most laboratories, and have better accuracy. What's more, this study will also give us more understanding of the relationship between the PL characteristics and ferroelectric phase structure, which is important for future applications of ferroelectrics as multifunctional materials. To our knowledge, little work has been done in this field. In fact, we only know of two research papers that discuss the PL change around T_C [12,15]. However, both these only investigated the PL peak intensity, which is semi-quantitative and easily affected by environmental and measurement conditions. The peak position, however, is an intrinsic quantity that reflects the energy level structure and is seldom influenced by the environment and measurement. We expect optimum results by simultaneously monitoring the change in the peak position and intensity through the phase transitions of the ferroelectric.

As one of the most studied RE ions, Er^{3+} has been widely investigated as an upconversion (UC) PL center [16–19]. The UC

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* Corresponding author. Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150080, China.
** Corresponding author. Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150080, China.
E-mail addresses: zhangzhiguo@hit.edu.cn (Z. Zhang), dzk@psu.edu (W. Cao).

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mechanism of this ion and its PL features have been characterized. $Ba_xCa_{1-x}TiO_3$ (BCT) ceramics have drawn considerable attention for their excellent optical properties as luminescent hosts and for their photorefractive properties [20–23]. In this work, we chose Er^{3+} as the PL center and doped it into a typical ferroelectric, $Ba_{0.77}Ca_{0.23}TiO_3$ ceramic. The hysteresis loop was measured to determine if doping influenced the ferroelectricity. The PL peak at 547 nm, originating from $^4S_{3/2}$ to $^2I_{15/2}$ transitions, was investigated and found to be extremely sensitive to crystal symmetry change caused by the phase transition. We determined the relationship between the intensity and peak position of the PL and the phase transition around T_C. We successfully measured T_C based on the PL critical behavior. The dielectric temperature spectrum was also recorded to measure T_C for comparison with the newly developed PL method.

2. Methods

A 1 mol% Er^{3+} doped BCT ceramic was prepared by the sol-gel method. Barium acetate ($Ba(CH_3COO)_2$), calcium acetate ($Ca(CH_3COO)_2$), tetrabutyl titanate ($TiC_{16}H_{36}O_4$), and erbium nitrate solution ($Er(NO_3)_3$) were used as raw materials. Absolute ethyl alcohol and glacial acetic acid were used as solvents. $Ba(CH_3COO)_2$, $Ca(CH_3COO)_2$, and $Er(NO_3)_3$ were first dissolved in a solution of glacial acetic acid and deionized water, according to the stoichiometric ratios. The solution was stirred for 0.5 h at 323 K, and then, tetrabutyl titanate was dissolved in a separate solution of absolute ethyl alcohol and glacial acetic acid. While all the solutions were cooled to room temperature, the former solution was added dropwise to the latter. The resulting solution was stirred at 333 K. After 0.5 h, a clear gel was formed. This precursor was dried in an oven at 353 K for 12 h and then calcined at 1173 K for 3 h. The resulting powders were pressed into disk pellets and sintered at 1673 K for 4 h. The samples were coated with silver paste and fired at 823 K for 0.5 h for ferroelectricity and piezoelectricity testing. Then, the sample was polished for optical tests.

The crystal structure of the ceramic was identified by X-ray diffraction (XRD) with an automated Rigaku D/max 2400 X-ray diffractometer using CuKα radiation. The hysteresis behavior was studied at room temperature using a Precision Premier II Ferroelectric Tester. The dielectric constant of the ceramic was measured using an automatic measuring system with an Agilent E4980A impedance analyzer. The PL spectra of the sample at different temperatures from 323 K to 423 K were measured with a Zolix Omni-λ 300 spectrometer under excitation from a 980-nm diode laser. A LINKAM stage was employed for temperature control. To ensure accuracy, the same heat/cold stage was used both for PL spectra and dielectric spectra detection.

3. Results and discussions

The XRD pattern of the prepared sample is shown in Fig. 1. The sample can be clearly identified as a tetragonal phase $BaTiO_3$ structure (PDF#05-0626). The diffraction peak shifts to slightly bigger angles, because the radii of the dopant Ca^{2+} ions and Er^{3+} ions are much smaller than those of the Ba^{2+} ions; hence, the interplanar spacing is decreased. The ferroelectric hysteresis loop along with the electric field was recorded to determine whether the ferroelectricity of the host material is affected by the dopant Er^{3+} ions. The remnant polarization P_r is 11 μC/cm2; the maximum polarization P_{max} is 14 μC/cm2; and the coercive field E_c is 7 kV/cm. These results are summarized in Fig. 2. The ferroelectricity was nearly unchanged compared with that of the pure BCT ceramics. Based on the facts above, it can be concluded that slight doping of rare earth ions into the ferroelectric host will not change the ferroelectricity, and the Er^{3+} ions are well doped into the crystal lattice, as designed. Hence, it is necessary for us to investigate the PL critical characteristics in BCT ceramic and the relationship between PL and the phase transition.

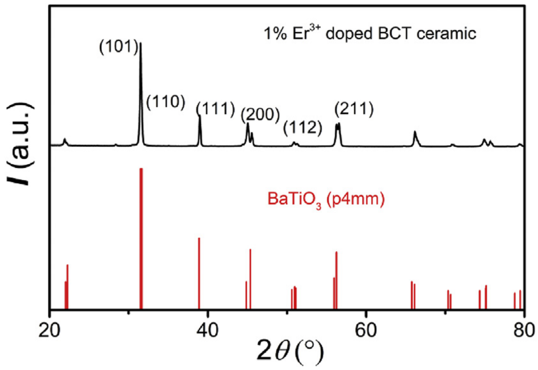

Fig. 1. XRD pattern of Er^{3+}-doped BCT ceramic.

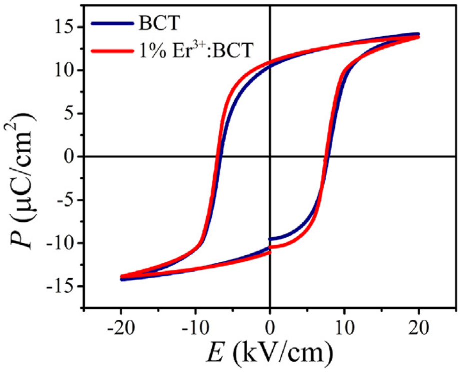

Fig. 2. Polarization hysteresis loop vs. electric field of Er^{3+} doped BCT ceramic.

The Er^{3+}-doped BCT ceramic exhibits strong green UC PL with a 980-nm diode laser as the excitation source. Fig. 3(a) shows the PL spectrum of the $^4S_{3/2}$ to $^4I_{15/2}$ transition of the sample at 373 K. Due to the low symmetry of the host crystal field, the transition was split into four sub-peaks by the Stark effect. For convenience, the four peaks are labeled as peak 1, 2, 3, and 4 in Fig. 3(a). The UC mechanism is plotted in Fig. 3(b). The 980-nm diode laser excitation pumps the Er^{3+} ions in the BCT ceramic from the ground state to the first excited state, $^4I_{11/2}$ (GSA). Energy transfer (ET) with another Er^{3+} ion transitions can populate the Er^{3+} ion in $^4I_{11/2}$ state to the $^4F_{7/2}$ excited state. The transition to the $^4F_{7/2}$ state can also occur because of the absorption of another laser photon through excited state absorption (ESA). Eventually, the Er^{3+} ions in the $^4F_{7/2}$ state drop down to the $^4S_{3/2}$ states through a non-radiative relaxation process. This is the mechanism by which the $^4S_{3/2}$ states are populated. The PL we discuss in this paper originates from the transition from $^4S_{3/2}$ excited states to $^4I_{15/2}$ ground states.

We then analyzed the PL characteristics in the temperature range of 353 K–423 K where the Curie phase transition is supposed to occur. We found that the PL is extremely sensitive to the lattice structure. Fig. 4(a) reveals the total integral area of the peak intensity originating from the $^4S_{3/2}$ state to $^2I_{15/2}$ state transition. It is interesting to see there is a dramatic change in the intensity as a function of temperature. The intensity variation can be divided into two parts, i.e., at temperatures below 381 K and above 381 K. When the temperature is below 381 K, the PL attenuates slowly with increasing temperature. This slow intensity decline is primarily explained by changes in crystal symmetry. The host BCT ceramic