Enhanced scintillation of $Ba_3In(B_3O_6)_3$ based on nitrogen doping

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ABSTRACT

Scintillating materials, as a class of luminescent materials, are highly demanded for practical use in the high-energy detection. However, the applications are often hampered by their low light yield (LY) or long decay time for many traditional scintillators. In this work, upon nitrogen anion doping, scintillation performance in layered borate $Ba_3In(B_3O_6)_3$ (BIB) has been excellently enhanced with high XEL intensity of ~3 times as large as that of commercial $Bi_4Ge_3O_{12}$ (BGO) and ultra-fast fluorescent decay time of ~1.25 ns. To shed light on origins of the intrinsic violet-blue emission, we measured the in-situ vacuum ultraviolet excited (VUV) emission spectra of N-BIB ceramic. Combined with experiments and first principles calculations, the band-gap reduction and donor-acceptor density increasing by nitrogen (N) doping is responsible for the enhancement of scintillation performance for N-doped $Ba_3In(B_3O_6)_3$. Moreover, nitrogen anion doping rather than conventional cation doping is found to be also applicable to other intrinsic luminescent materials for enhancing performance.

1. Introduction

Radiation detectors are widely used in high-energy physics, irradiation medicine, well logging and safety scanning. The performance of a radiation detector mainly relies on scintillator's properties, especially on light yield (LY) and decay time [1,2]. According to the origin of luminescence, scintillating materials can be divided into two categories: extrinsic scintillators with activator ions (such as Yb^+, Ce^{3+}, and Eu^{2+}) and intrinsic scintillators [3] without activator ions. Owing to the comparatively-slow de-excitation of activator ions and high melting points, extrinsic scintillators usually suffer long decay time, difficulty in crystal growth and comparably high cost in spite of their high LY (e.g., $Lu_3Al_5O_{12}$:Yb and Lu_2SiO_5:Ce) [4,5]. This is unacceptable for fast imaging with fast time resolutions. Of special interest are the intrinsic scintillators which can theoretically possess a fast decay time in the order of 1 ns[3]. However, there remains much room for enhancement since even the most widely used commercial intrinsic scintillators have their drawbacks. For example, $Bi_4Ge_3O_{12}$ (BGO) has a high LY (~8000 ph/MeV) but with a slow decay time (~300 ns) [1,6]; While, due to the low LY (~100 ph/MeV), $PbWO_4$ (PWO) is restricted its application to high-energy physics, in spite of its very fast decay time (~10 ns) and high density for intensive applications in electromagnetic calorimeters and photon detectors [7]. For intrinsic scintillator, the luminescence is usually sensitive to structure factors including crystal structure, oxygen composition and impurities. For example, Feng [8] reported the influence of lattice defects on performance of PWO scintillators. Impurities at different lattice sites have significant effects on optical properties of materials [9]. Over the past few decades, extensive studies on LY enhancement of scintillators by cation doping [10–17] have been carried out, but only a few on anion doping. In Ren's work [18], fluorine anion was used as dopant to improve the light output of PWO crystal. The most significant characteristic of the F-doped PWO is that two emission components can be identified in their photoluminescence spectra, a fast component related to the blue emission (419 nm) and a slow one related to the green emission (553 nm). The light yield of PWO:F is ~2 times as high as of the undoped PWO. The significant contribution to the light yield of PWO may come from the green luminescence. However, the total scintillating light decay of PWO:F is extended to ~50 ns due to the slow component induced by F-anion. It is reported that oxide introduces nitrogen at oxygen sites and creates oxygen vacancies for charge-balanced incorporation and thus has a significant effect on electronic structure [19]; however, their possible effect on scintillation performance has been rarely studied so far.

Owing to their rich crystal-structure types, wide transmittance spectra and wide band gaps, borates are well known as promising optical functional materials [20–32]. In 2008, we investigated sub-solidus phase relationship in $BaO-In_2O_3-B_2O_3$ system, leading to the

discovery of two ternary compounds, $Ba_3In(B_3O_6)_3$ (BIB) and $Ba_3In(BO_3)_3$. It was found that layered structure BIB is a potential intrinsic scintillation material [33]. Recently, thermal stability, phase transition mechanism, primary crystal region, and thermodynamic parameters for the layered borate BIB were determined, which will help grow crystals of BIB [34,35]. Very recently, Wang's group reported its short optical absorption edge and high transmittance of BIB crystal [36].

In this contribution, the scintillation property of BIB ceramic is found sensitive to lattice defects. Here, we report the significant enhancement of scintillation properties of BIB ceramic using a facile method. The BIB upon nitrogen doping (N-BIB) has the improved LY being about 3 times as large as that of commercial BGO, along with ultra-fast fluorescent decay time (~ 1.25 ns). By experiments and first principles calculations, present work demonstrates that nitrogen doping effectively narrows the band gap, enlarges photon absorption, and thus greatly enhance scintillation properties. Moreover, this doping route is expected to be also applicable to improvement of scintillating property for commercial BGO.

2. Methods

2.1. Samples synthesis

Barium carbonate ($BaCO_3$) (99.99% metals basis, CAS No. 513-77-9), indium oxide (In_2O_3) (99.99% metals basis, CAS No. 1312-43-2), and boric acid (H_3BO_3) (99.99% metals basis, CAS No. 10043-35-3) were purchased from Alfa Aesar. The BIB sample was synthesized by melting and crystalline method. Firstly, stoichiometric raw materials were finely ground into powders in a mortar of agate. Secondly, the mixtures were putted in platinum crucible and preheated in air at ~ 600 °C for 12 h, and naturally cooled to room temperature. Then, they were reground and melted at ~ 1200 °C for 12 h. Subsequently, the melting samples were transfer into a furnace to crystallize at ~ 900 °C for 24 h. In all cases, care was taken to add extra ~ 0.2 mol% H_3BO_3 in order to offset the weight losses of B_2O_3 in the procedure of synthesis. The N-BIB sample was prepared by urea treatment. Urea were placed separately in a two-zone tube furnace with BIB and annealed at ~ 500 °C for 5 h under argon atmosphere. The control sample was treated the same but without urea to achieve similar crystallinity. BGO samples were provided by Shanghai Institute of Ceramics (Chinese Academy of Sciences). Follow the same urea treatment described above, the nitrogen doping into BGO was achieved.

2.2. X-Ray diffraction

Powder X-Ray diffraction data were recorded on an X-ray diffractometer (Rigaku D/Max-2500) with Cu Kα radiation and a diffracted-beam graphite monochromator operated at a power of 40 kV and 150 mA. Inorganic Crystal Structure Database (ICSD released 2016) and the Powder Diffraction File (PDF released 2012) were used for phase analysis for the samples.

2.3. X-ray photoelectron spectra

X-ray photoelectron spectra measurements were performed using an ESCALAB- 250Xi X-ray photoelectron spectrometer.

2.4. Nitrogen contents measurements

For a determination of the nitrogen contents in N-BIB, the sample was subject to nitrogen analysis using a LECO TC-600 analyzer.

2.5. X-ray excited emission spectroscopy

In practical scintillation detectors, there are two kinds such as the photon counting (pulse height) and the integrated types. Generally, the fast scintillation response of single crystal is required in the former one. As for scintillation ceramic samples, there are many successful cases using the latter type. In this work, X-ray excited emission spectra were recorded at room temperature on a home-made spectrometer SicOmni-X composed of a F50-100II mobile X-ray unit using tungsten target (75 kV, 50 mA) and a Hamamatsu R928-28 electron-multiplier photo-tube ascribed to the integrated radioluminescence (RL) spectrum. The spectrometer is corrected by Hg lamp LHM254. All powder samples were sintered to tablet before performed the measurements.

2.6. In-situ vacuum ultraviolet (VUV) excited emission spectroscopy

In-situ vacuum ultraviolet excited emission spectra were conducted at VUV spectroscopy station (Beijing Synchrotron Radiation Facility).

2.7. Decay constant measurements

Time-resolved emission decay behaviors were measured at room temperature on an Edinburgh Instruments Ltd. Spectrometer (FLS920, England) with nF Lamp as the excitation source and a R928-PA photomultiplier for signal detection.

2.8. Ultraviolet-visible absorption spectra

The UV absorption spectra were measured at room temperature through an SHIMADZU/UV-2600 ultraviolet spectrophotometer using an integrating sphere.

2.9. First principles calculations

A first principles study of the electronic structure for BIB was presented by using the scalar relativistic all-electron Bloch's projector augmented wave method within the generalized gradient approximation (GGA) [37], as implemented in the highly efficient Vienna ab initio simulation package (VASP) [38,39]. For the GGA exchange-correlation potential, the Perdew-Burke-Ernzerhof parameterization (PBE) [40] is employed. The k-point meshes for Brillouin zone sampling were constructed using the Monkhorst-Pack scheme [41], and the reciprocal space meshes are increased to achieve convergence to a precision of better than 1 meV/at. The plane-wave kinetic-energy cutoff is setted as 600 eV for all calculations. We have optimized the structure by minimization of the forces acting on the atoms. Once the forces are minimized in this construction one can then find the self-consistent density at these positions by turning off the relaxations and driving the system to self-consistency. We take the full relativistic effects for core states and use the scalar relativistic approximation for the valence states.

3. Results

3.1. Structure characterization

The powder XRD pattern for N-BIB, compared with that of undoped BIB, matches well with the $Ba_3In(B_3O_6)_3$ phase (ICSD #245820) (Fig. 1a) with no trace of any impurity, suggesting high purity of samples with possible N-doping. According to element characteristics and structure feature of the layered BIB [34], N is expected to replace an oxygen atom to form N_O in the lattice of BIB by urea treatment, as shown in Fig. 1b.

The nitrogen doping is confirmed by an additional N 1 s peak of N-BIB in X-ray photoelectron spectroscopy (XPS), compared with undoped BIB sample (Fig. 2a). The binding energy (399.7 eV) of the observed N 1 s peak is in excellent agreement with that in nitrogen-doped $BiVO_4$ [19]. The Ba 3d and In 3d peaks of N-BIB (Fig. 2b and c) are also shown in the XPS spectra with a little lower binding energy