Syntheses, characterization and nonlinear optical properties of a bismuth subcarbonate Bi$_2$O$_2$CO$_3$

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Abstract

A novel nonlinear optical (NLO) material Bi$_2$O$_2$CO$_3$ has been successfully developed by the hydrothermal method. It was characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectra, high resolution transmission electron microscopy (HRTEM), UV–vis–NIR diffuse reflectance spectrum (DRS) and photoluminescence (PL) spectra. The band gap was determined to be 3.42 eV, and the PL properties of Eu$^{3+}$ doped Bi$_2$O$_2$CO$_3$ under UV excitation have also been investigated. The powder second-harmonic generation (SHG) measurement performed on the ground crystal indicates that the NLO efficiency is approximately 5 times as large as that of KDP (KH$_2$PO$_4$) standard. In addition, the origin of large SHG for Bi$_2$O$_2$CO$_3$ was also researched according to its crystal structure.

1. Introduction

Nonlinear optical (NLO) materials have received much attention due to their significant applications in the laser field, including laser micromachining, semiconductor photolithography, photochemical synthesis and high-resolution photoemission spectrometer [1–5]. Among the numerous discovered NLO materials, borates exhibit the most promising application prospects in short wavelength region [6–12]. Especially, the planar [BO$_3$] groups with p-orbitals conjugated system as basic building units could produce a large microscopic second-order susceptibility and moderate birefringence. The representative examples include KBe$_2$BO$_3$F$_2$ family [13–15], Sr$_2$Be$_2$B$_2$O$_7$ [16] and YAl$_3$(BO$_3$)$_4$ [17]. Analogously, [CO$_3$] groups with the similar planar configuration are expected to be good NLO-active anionic groups to construct new NLO materials as well. Recently, the discovery for non-centrosymmetric compounds containing [CO$_3$] groups has been very active [18–20]. Besides, the compounds possessing p-cations with stereochemically active lone pairs, i.e., Bi$^{3+}$ and Pb$^{2+}$, may also make large contributions to the SHG effect [21–23]. Through the combination of [CO$_3$] groups and cations with lone pair electrons, we have obtained a new NLO material Bi$_2$O$_2$CO$_3$.

2. Experimental section

2.1. Synthesis and crystal growth

The bismutite (Bi$_2$O$_2$CO$_3$) was first reported by Grice’s group, and its non-centrosymmetric structure has been determined [24]. However, to our knowledge, the studies focused on the optical properties of Bi$_2$O$_2$CO$_3$, particularly for the photoluminescence and second-order NLO properties, have not been reported. In addition, further understanding of the relationship between the structure and the properties, especially the effects on NLO properties by coupling of [CO$_3$] groups and Bi$^{3+}$, is of interest and needs to be proved. In this article, we present the synthesis, structure and characterization of Bi$_2$O$_2$CO$_3$.

The syntheses of Bi$_2$O$_2$CO$_3$ were carried out in closed Teflon autoclaves. The starting materials, Bi(NO$_3$)$_3$·5H$_2$O and Urea, are of analytical grade and used as purchased without further purification. Bismuth nitrate Bi(NO$_3$)$_3$·5H$_2$O (5 mmol), Urea (CH$_4$N$_2$O, 8 mmol) and 1 mL purified water were well mixed, and then transferred into a 15 mL Teflon autoclave. The products were washed with ethanol and distilled water several times and dried at 80 °C for 4 h, subsequently. The Bi$_2$O$_2$CO$_3$ nanocrystals were formed after the autoclave was heated at 180 °C for 24 h. When the autoclave was heated at 200 °C for 10 d under autogenous pressure, the...
single crystals in millimeter level were obtained (Fig. S1). Eu$^{3+}$ doped Bi$_2$O$_2$CO$_3$ were synthesized using the same procedure when 5% Bi(NO$_3$)$_3$·5H$_2$O replaced by Eu(NO$_3$)$_3$·6H$_2$O. To further confirm the substitution of Eu ion and the doping concentration, ICP elemental analyses were performed on the as-prepared Eu–Bi$_2$O$_2$CO$_3$ samples. The results showed the molar ratio of Eu$^{3+}$/Bi$^{3+}$ is 1:18.6, which is in accordance with the expected values.

2.2. Structure characterization

X-ray diffraction (XRD) spectroscopy for phase identification was studied on a Bruker D8 ADVANCE X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The scanning step width of 0.02° and the scanning rate of 0.2° S$^{-1}$ were applied to record the patterns in the 2θ range of 10–70°. The XRD data for structural refinements were collected at ambient temperature using a PANalytical powder X-ray diffractometer XPert Pro with Cu-Kα radiation (40 kV, 40 mA). The data was collected over a 2θ range from 10° to 120° at intervals of 0.017° with a counting time of 1 s per step. The microstructure was obtained by a JEM-2100F high resolution transmission electron microscopy (HRTEM). The Fourier transform infrared (FTIR) spectrum was recorded in the range 400–4000 cm$^{-1}$ using the Shimadzu IR Affinity-Infrared spectrometer. The sample was mixed thoroughly with dried KBr (5 mg sample and 500 mg KBr). A Varian 710-ES (USA, Varian) inductively coupled pI0asma optical emission spectrometer (ICP-OES) with Sepex Certiprep standards was employed to analyze the elements of the samples.

2.3. Diffuse-reflectance spectroscopy

A Cary 5000 UV—visible—NIR spectrophotometer with a diffuse-reflectance accessory was used to measure the spectrum of Bi$_2$O$_2$CO$_3$ over the range 200 nm (6.20 eV) to 900 nm (1.38 eV).

2.4. Luminescence measurements

Photoluminescent spectrum of the sample was carried out at room temperature by a JOBIN 10 YVON FluoroMax-3 fluorescence spectrophotometer. In order to fully evaluate the luminescence performance of the sample, excitation spectrum was measured in the range of 200–550 nm, and the emission spectrum was recorded in the range of 400–850 nm.

2.5. SHG measurements

SHG tests were performed on ground crystals of Bi$_2$O$_2$CO$_3$ by means of the Kurtz–Perry method [25]. The sample was irradiated with a pulsed infrared beam (10 ns, 3 mJ, 10 kHz) produced by a Q-switched Nd:YAG laser at wavelength of 1064 nm. As powder SHG effect depends strongly on the particle size, Bi$_2$O$_2$CO$_3$ crystals were ground and sieved into the following particle size ranges: 35–50, 50–74, 74–105, and 105–150 μm, respectively. Microcrystalline KH$_2$PO$_4$ (KDP) samples within the corresponding size ranges served as the standard.

3. Results and discussion

3.1. Structure and microstructure of Bi$_2$O$_2$CO$_3$

Bi$_2$O$_2$CO$_3$ crystallizes in the orthorhombic space group Imm2, the crystal structure was shown in the left of Fig. 1. It was constructed by (Bi$_2$O$_2$)$_2$$^{3+}$ layers and isolated [CO$_3$] planar groups. The (Bi$_2$O$_2$)$_2$$^{3+}$ layers are always found in many Bi-based compounds with Aurivillius structure and Sillén structure [26,27]. In the structure of Bi$_2$O$_2$CO$_3$, (Bi$_2$O$_2$)$_2$$^{3+}$ layers and [CO$_3$] layers are
intergrown with the plane of the [CO3] group orthogonal to the plane of the (Bi2O2)2+ layer. The segregated “standing-on-end” carbonate layer can be clearly seen in the crystal structure. From the right of Fig. 1, we can see the two kind of Bi atoms are all eight coordinated. From Fig. 2, we can see that the X-ray powder diffraction pattern of sample and the theoretical simulation of the single-crystal crystallographic data from Inorganic Crystal Structure Database (ICSD) are in good accordance, indicating the formation of pure phase. Fig. 3 gives the Rietveld analysis patterns for X-ray powder diffraction data of Bi2O2CO3. The lattice parameters are refined to \( a = b = 3.8658(5) \, \text{Å}, \) and \( c = 13.6757(5) \, \text{Å} \). The reliability parameters of refinement are \( R_{wp} = 10.9\% \), \( R_p = 7.89\% \), \( \chi^2 = 5.49 \), which can further verify the phase purity of the as-prepared sample.

To investigate the microstructure and further confirm the crystallization phase, high resolution transmission electron microscopy (HRTEM) has been performed. The lattice resolved HRTEM image in Fig. 4 showed the spacing of the lattices are 0.273 nm and 0.342 nm, which are in agreement with the spacing of [110] and [004] crystallographic planes of Bi2O2CO3, respectively. It is apparent that Bi2O2CO3 single crystals were successfully synthesized.

The infrared spectrum measurement was performed to confirm the anionic groups of Bi2O2CO3. Fig. 5 shows the complete spectral region of the infrared spectrum between 500 and 4000 cm\(^{-1}\). The peaks observed in the 1400 cm\(^{-1}\) and 1450 cm\(^{-1}\) can be attributed to the antisymmetrical stretching mode of CO3 group, and the bending modes of triangular CO3 group gives rise to the absorption peaks at 848 cm\(^{-1}\). These peaks observed are in good accordance with that of other carbonates [28].
3.2. Diffuse-reflectance spectroscopy

The UV–vis–NIR diffuse reflectance spectrum of Bi$_2$O$_2$CO$_3$ in the region of 200–2500 nm was shown in Fig. 6. Absorption $(K/S)$ data were calculated from the following Kubelka–Munk function [29]:

$$F(R) = \left(1 - R^2\right)/2R = K/S,$$

where $R$ is the reflectance, $K$ is the absorption, and $S$ is the scattering. It is clear that there is no significant absorption in the region between 220 and 900 nm, which indicating that this compound may have potential applications as UV NLO material.

Furthermore, the band gap of Bi$_2$O$_2$CO$_3$ was also obtained. In semiconductors, the square of absorption coefficient is linear with energy for direct optical transitions in the absorption edge region; whereas the square root of absorption coefficient is linear with energy for indirect transitions [27]. Because of the direct optical transition property of Bi$_2$O$_2$CO$_3$ [30], data plots of absorption$^2$ versus energy in the absorption edge region has been shown in the inset of Fig. 6, which indicates the band gap of Bi$_2$O$_2$CO$_3$ is 3.42 eV.

3.3. Luminescence spectroscopy

Fig. 7 shows the excitation and emission spectra of Bi$_2$O$_2$CO$_3$ at room temperature. The excitation spectrum of Bi$_2$O$_2$CO$_3$ monitoring the emission at 613 nm is shown on the left of Fig. 7. It is characterized by absorption bands at 363, 383, 394 and 416 nm, which are assigned to Eu$^{3+}$ electronic transitions $^5D_0 \rightarrow ^7D_4$, $^7F_2 \rightarrow ^5L_6$, $^7F_0 \rightarrow ^5L_4$ and $^7F_0 \rightarrow ^5D_3$, respectively. Since the maximum absorption is at 394 nm, it is fixed as excitation wavelength for recording the emission spectra. This emission spectrum shows that the emission bands are assigned to the electronic transitions $^5D_0 \rightarrow ^7F_0$ at 581 nm, $^5D_0 \rightarrow ^7F_1$ at 593 nm, $^5D_0 \rightarrow ^7F_2$ at 614 nm and $^5D_0 \rightarrow ^7F_3$ at 652 nm. The dominant emission peak centered at 614 nm are resulted from the electric dipole (ED) $^5D_0 \rightarrow ^7F_2$ transition of Eu$^{3+}$, which are stronger than the band at 593 nm from magnetic dipole (MD) $^5D_0 \rightarrow ^7F_1$ transition. These findings suggest that Eu$^{3+}$ ions locate on sites with anti-inversion symmetry, which is consistent with the structural data [31].

3.4. Nonlinear optical properties

Because of the noncentrosymmetric structure of Bi$_2$O$_2$CO$_3$, it is expected to possess NLO properties. The curves of the powder SHG signals as a function of particle size were detected and compared with that of KDP. Our measurements showed that Bi$_2$O$_2$CO$_3$ has a very large SHG effect which was about 5 times that of KDP. Fig. 8 shows the relationship between the particle size and SHG effect of Bi$_2$O$_2$CO$_3$. As can be seen, the SHG effects are not proportional to the particle size. It means that the Bi$_2$O$_2$CO$_3$ crystal may not support phase-matching of SHG in the visual region.

According to the anionic group theory of NLO activity in borates [32–34], the planar [BO$_3$] units with $\pi$-orbitals possess a large microscopic second-order susceptibility. Thus, the [CO$_3$] groups having the similar planar structure with $\pi$-orbitals will also provide a large microscopic second-order susceptibility. Moreover, one can easily find that the large cation Bi$^{3+}$ shows stereo active lone-pair behaviors along the $c$-axis that may result in the large distortion of Bi–O polyhedron, which also make large contributions to the SHG effect. Therefore, the sum of the contributions from both the [CO$_3$] groups and (Bi$_2$O$_2$)$_2$ layers results in the very large NLO effect observed in Bi$_2$O$_2$CO$_3$.

4. Conclusion

In summary, the combination of [CO$_3$] groups and Bi$^{3+}$ cations with lone pair electrons results in a new NLO material Bi$_2$O$_2$CO$_3$. The single crystals were obtained by hydrothermal method. The crystal structure was confirmed by XRD and HRTEM, and the [CO$_3$] functional groups present in the sample were identified by FTIR spectrum. The UV–vis–IR diffuse reflectance spectrum showed that this compound has a band gap of 3.42 eV. Under the excitation at 394 nm, the Eu$^{3+}$ doped Bi$_2$O$_2$CO$_3$ displays the strongest red emission peak of $^5D_0 \rightarrow ^7F_2$ located at 613 nm, which is in good agreement with the noncentrosymmetric symmetry. SHG measurement demonstrated that the compound exhibits a NLO effect about 5 times that of KDP. The large NLO effect comes from both the planar [CO$_3$] groups and the lone pair electrons of Bi$^{3+}$ ions. Our results provide a new approach to the exploration of novel NLO materials.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.solidstatesciences.2014.01.010.

References