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# Novel BaTeMo<sub>2</sub>O<sub>9</sub> fine particles synthesized via a supercritical water route<sup>†</sup>

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Pure-phase BaTeMo<sub>2</sub>O<sub>9</sub> polycrystals with uniform particle shape and size have been successfully synthesized in a supercritical water system and the novel optical properties were reported.

Oxide compounds are one class of the most essential and important materials due to their diverse and powerful functions including acoustic, optical, electrical and magnetic, thermal performance. According to the number of component elements, they are classified into binary oxides, ternary oxides and quaternary oxides. Up to now much work has been done on binary and ternary oxide materials, and interest has already switched to homogenization, microminiaturization and even commercial applications.<sup>1</sup> In contrast, because of the structure complexity and limitations of the synthetic process, quaternary oxide particles with single phase and uniform morphology have been seldom prepared until now.<sup>2</sup>

BaTeMo<sub>2</sub>O<sub>9</sub> (BTM) is an attractive noncentrosymmetric (NCS) oxide material, containing both d<sup>0</sup> transition metal cations (Mo<sup>6+</sup>) and cations with nonbonded electron pairs (Te<sup>4+</sup>) susceptible to the second-order Jahn-Teller (SOJT) effect. The BTM compound that crystallizes in a NCS monoclinic crystal system with space group  $P2_1$ , was first synthesized by Halasyamani's group in 2003, and the bulk crystal was successfully grown by Tao and co-workers in 2008.<sup>3</sup> However, to the best of our knowledge, a traditional solid-state method is still the only way to synthesize BTM compounds, in which high-temperature treatment might result in serious aggregation and lack of particle uniformity. Thus there have not been any reports on its particle morphology. However, we believe that BTM polycrystals with uniform morphology might offer exciting opportunities for both fundamental research and technological applications. Therefore, it is necessary to explore an innovative and feasible method to synthesize pure BTM polycrystals with uniform morphology.

In recent years, studies on the application of supercritical fluids have developed very rapidly owing primarily to their special chemical and physical properties.<sup>4</sup> Particularly, supercritical water with a temperature higher than 373.15 °C and a pressure higher than 22.1 MPa has proved to be an effective and environmentally benign reaction medium for the synthesis of multicomponent oxide compounds with pure phase and high crystallinity.<sup>5</sup> Compared with the solid-state method, reactions in supercritical water occur at lower temperature in a shorter time. Especially the supercritical water process has the great advantage of being able to modify and improve the morphology of multicomponent oxide materials.<sup>4</sup>

In this communication, we report the synthesis of single-phase  $BaTeMo_2O_9$  polycrystals with regular shape and size through a one-step process in a supercritical water system. Its optical properties were explored. In addition, the comparison between the fine BTM particles and those prepared by the solid-state method are discussed.

In the experiment, the starting materials including potassium hydroxide aqueous solution (AR, KOH, 0.1 M, 15 ml), barium nitrate aqueous solution (AR, Ba(NO<sub>3</sub>)<sub>2</sub>, 0.1 M, 15 ml), tellurium oxide powders (99.99%, TeO<sub>2</sub>, 0.2394 g, 1.5 mmol), molybdenum oxide powders (99.99%, MoO<sub>3</sub>, 0.4379 g, 3 mmol), and 20 ml deionized water were mixed together in a fixed order. After continuous stirring for 30 min, the mixture was placed into a gold-lined high-temperature and high-pressure autoclave. (Detailed information about this apparatus is in the ESI<sup>+</sup>) The reaction process was carried out at 380 °C with an autogenous system pressure (around 24 MPa) for 1 h. Upon completion of the reaction, the autoclave was opened after the whole system cooled naturally to room temperature. Light vellow precipitates inside were collected, washed with distilled water, and then dried at 50 °C. As a comparison, polycrystalline BaTe-Mo<sub>2</sub>O<sub>9</sub> was synthesized by solid-state reaction techniques described previously.3b

The products were characterized by means of X-ray powder diffractometry (XRD; Bruker D8 ADVANCE, Cu-K $\alpha$  radiation, 40 kV and 40 mA), scanning electron microscopy (SEM; Hitachi S-4800), high resolution transmission electron microscope (HRTEM; JEOL JEM-100CXII, operating at 200 kV), X-ray photoelectron spectroscopy (XPS; Thermofisher Scientific ESCALAB 250), measurement of nonlinear optical property (Q-switched laser, Beamtech SGR10, output wavelength at 1053 nm, pulse width at 18 ns), UV-vis absorption spectra (Shimadzu UV-2550), and fluorescence spectrum (Edinburgh FLS920, equipped with a 450 W Xe lamp and a time-correlated single photon counting card).

Fig. 1 shows the XRD patterns of the BaTeMo<sub>2</sub>O<sub>9</sub> powders synthesized in the supercritical water system. All the diffraction peaks of the XRD pattern match with the standard data calculated from the bulk crystal grown by Tao *et al.*,<sup>3b</sup> indicating that the crystallographic phase of these particles belongs to the monoclinic phase (space group:  $P_2_1$ ). No characteristic peaks of raw materials or other impurities, such as MoO<sub>3</sub>, TeO<sub>2</sub>, BaMoO<sub>4</sub> are observed in the XRD pattern. Thus, the synthesis route using supercritical water has proved to be successful and efficient to synthesize single-phase BTM compounds with high crystallinity.

Fig. 2 displays SEM images of the BTM particles obtained by supercritical water process (Fig. 2a, 2b and 2c) and a solid-state method (Fig. 2d), respectively. According to Fig. 2a, 2b, and 2c, it is obvious that the particles synthesized in supercritical water mainly consist of uniform micron-sized plates, with lengths and widths around 10  $\mu$ m and thicknesses of 0.5–1.0  $\mu$ m. Through a delicate observation, it is interesting to find that side faces of the individual plates are hexagonal, which is similar to the ideal morphology of

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Fig. 1 XRD pattern of BTM powders synthesized in the supercritical water system, compared with standard data shown by the lines at the bottom.



**Fig. 2** SEM images of BTM particles synthesized (a), (b) and (c) in the supercritical water system, (d) by the solid-state reaction.

BTM bulk crystal reported before.<sup>36</sup> Nevertheless, BTM polycrystalline particles synthesized by the solid-state method exhibit an irregular shape and an uneven size distribution, which is shown in Fig. 2d. Considering the vast difference between Fig. 2a, 2b, 2c and Fig. 2d, it is demonstrated that BTM particles with single phase and uniform morphology have been successfully prepared in the supercritical water system.



**Fig. 3** HRTEM images of synthesized BTM micro-plate particles. The inset of (a) is the SAED pattern.

Fig. 3a shows the HRTEM image and selected area electron diffraction (SAED) pattern of an individual BTM plate, confirming the single crystalline structure of the micro-plates. Fig. 3b is the lattice fringe image of a BTM plate. The distance between the lattice fringe is about 0.55 nm, which coincides with the *d*-spacing of the (100) lattice plane. Thus the direction of growth corresponds to the schematic representation of the crystal structure of BaTeMo<sub>2</sub>O<sub>9</sub>.

To provide further evidence for the formation of BTM particles, the sample was characterized by the XPS technique. In the XPS spectra shown in Fig. S2,† the peaks at 777.40 eV and 792.55 eV correspond to Ba 3d binding energy, 573.80 eV and 584.20 eV corresponds to Te 3d, 229.45 eV and 232.65 eV corresponds to Mo 3d, consistent with the composition elements of BaTeMo<sub>2</sub>O<sub>9</sub>. Quantification of the XPS peak intensities reveals that the ratio of Ba, Te and Mo is 1 : 1 : 1.9, which indicates the purity of the as-prepared BTM polycrystals.

Fig. 4 is the UV-Vis absorption spectra of the BTM particles synthesized in the supercritical water system and by using the solid-state reaction. The band gap of BTM particles synthesized in the supercritical water system is determined from the fundamental absorption edge of the spectra which is 3.28 eV, and larger than that obtained by the solid-state method (3.19 eV). The optical absorption edge and the optical band gap would be influenced by the shape and size of semiconductor materials.<sup>6</sup> In our experiment, BTM particles with uniform plate size possess the wider band gap.

The fluorescence spectrum of BTM particles synthesized in the supercritical water system is presented in Fig. 5. With the excitation wavelength at 320 nm, BTM particles exhibited three photoluminescence emission bands with peaks at 416 nm, 456 nm and 526 nm, respectively. This fluorescence of a BTM compound is the first observed and needs further research.<sup>7</sup>

Moreover, to characterize the nonlinear optical property of BTM particles, a laser with a 1053 nm output wavelength was used as the light source. Under irradiation with 1053 nm radiation green light was observed showing some nonlinear optical properties.

In summary, uniform single-phase BTM micro-plates were synthesized successfully through a supercritical water route for the first time. The size of the particles is around 10  $\mu$ m in length and width, and with a thickness of 0.5–1.0  $\mu$ m. The applications of BaTeMo<sub>2</sub>O<sub>9</sub> would be widely extended due to this novel and regular particle morphology, as well as the optical properties. Meanwhile, the supercritical water process provides a green, facile and effective way



**Fig. 4** UV-Vis absorption spectra of BTM particles synthesized (a) in the supercritical water system; (b) by the solid-state reaction.



Fig. 5 The emission spectra of BTM particles synthesized in the supercritical water system.

for synthesising more quaternary oxides powders with modified features.

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#### Notes and references

 (a) B. A. Hernandez, K. S. Chang, E. R. Fisher and P. K. Dorhout, *Chem. Mater.*, 2002, 14, 480; (b) L. Vayssieres, *Adv. Mater.*, 2003, 15, 464; (c) A. Tsukazaki, A. Ohtomo, T. Onuma, M. Ohtani, T. Makino, M. Sumiya, K. Ohtani, S. F. Chichibu, S. Fuke, Y. Segawa, H. Ohno, H. Koinuma and M. Kawasaki, *Nat. Mater.*, 2005, **4**, 42; (*d*) X. B. Chen and S. S. Mao, *Chem. Rev.*, 2007, **107**, 2091; (*e*) A. ikesue and Y. L. Aung, *Nat. Photonics*, 2008, **2**, 721.

- S. F. Yang, P. Y. Zavalij and M. S. Whittingham, *Electrochem. Commun.*, 2001, 3, 505; (b) B. Li, Y. Hakuta and H. Hayashi, *Chem. Commun.*, 2005, 1732; (c) D. Muñoz-Rojas, G. Subías, J. Oró-Solé, J. Fraxedas, B. Martínez, M. Casas-Cabanas, J. Canales-Vázquez, J. Gonzalez-Calbet, E. García-González, R. I. Walton and N. Casañ-Pastor, J. Solid State Chem., 2006, 179, 3883.
- 3 (a) H. S. Ra, K. M. Ok and P. S. Halasyamani, J. Am. Chem. Soc., 2003, **125**, 7764; (b) W. G. Zhang, X. T. Tao, C. Q. Zhang, Z. L. Gao, Y. Z. Zhang, W. T. Yu, X. F. Cheng, X. S. Liu and M. H. Jiang, Cryst. Growth Des., 2008, **8**, 304; (c) Z. L. Gao, X. T. Tao, X. Yin, W. G. Zhang and M. H. Jiang, Appl. Phys. Lett., 2008, **93**, 252906; (d) W. G. Zhang, X. T. Tao, C. Q. Zhang, H. J. Zhang and M. H. Jiang, Cryst. Growth Des., 2009, **9**, 2633.
- 4 (a) D. BrÖll, C. Kaul, A. Krämer, P. Krammer, T. Richter, M. Jung, H. Vogel and P. Zehner, *Angew. Chem., Int. Ed.*, 1999, 38, 2998; (b)
  M. Boero, K. Terakura, T. Ikeshoji, C. C. Liew and M. Parrinello, J. Chem. Phys., 2001, 115, 2219; (c) N. Akiya and P. E. Savage, Chem. Rev., 2002, 102, 2725; (d) H. Weingärtner and E. U. Franck, Angew. Chem., Int. Ed., 2005, 44, 2672.
- E. Reverchon and R. Adami, J. Supercrit. Fluids, 2006, 37, 1; (b)
   M. N. Danchevskaya, Y. D. Ivakin, S. N. Torbin and
   G. P. Muravieva, J. Supercrit. Fluids, 2007, 42, 419; (c) A. Kruse and
   E. Dinjus, J. Supercrit. Fluids, 2007, 39, 362; (d) R. G. Rodriguez,
   S. P. Mezyk, C. Stewart, H. W. Rollins, B. J. Mincher, R. V. Fox,
   B. Phillips and R. Brey, J. Phys. Chem. A, 2007, 111, 468; (e)
   Q. X. Zheng, B. Li, H. D. Zhang, J. J. Zheng, M. H. Jiang and
   X. T. Tao, J. Supercrit. Fluids, 2009, 50, 77.
- 6 (a) C. M. Joseph and C. S. Menon, J. Phys. D: Appl. Phys., 2001, 34, 1143; (b) L. Zhang, J. Liang, S. J. Peng, Y. H. Shi and J. Chen, Mater. Chem. Phys., 2007, 106, 296; (c) K. Goksen and N. M. Gasanly, Phys. B, 2007, 400, 266.
- 7 (a) Y. Toyozawa and M. Inoue, J. Phys. Soc. Jpn., 1966, 21, 1663; (b)
  Y. Zhang, N. A. W. Holzarth and R. T. Williams, Phys. Rev. B: Condens. Matter Mater. Phys., 1998, 57, 12738; (c) J. W. Yoon,
  J. H. Ryu and K. B. Shim, Mater. Sci. Eng., B, 2006, 127, 154; (d)
  T. Thongtem, A. Phuruangrat and S. Thongtem, J. Nanopart. Res., 2010, 12, 2287.