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Facile hydrothermal synthesis of single crystalline barium aluminate nanoplatelets

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Abstract : Synthesis of one-dimensional $BaAl_2O_4$ single crystalline nanoplatelets has been realized in this article. The nanoplatelets were synthesized by a facile hydrothermal treatment of mixed solution of barium nitrate and aluminum nitrate in the presence or surfactants. Post-growth annealing at high temperatures promotes the crystallization of the materials. The $BaAl_2O_4$ nanoplatelets reported by us may have significant implications in examining shape dependent phosphorescence properties and building functional nanodevices.

Keywords : Nanoplatelets; $BaAl_2O_4$; Hydrothermal.

INTRODUCTION

Nanoscale materials and structures, such as nanotubes, nanowires, nanobelts, and nanoplatelets have attracted much research attention in the past decade due largely to their significant implications in basic physical and chemical properties and potential applications in fields including optoelectronics, sensors, field emission, bioassay, and so on[1-5]. So far, many one-dimensional materials have been synthesized by a lot of well studied approaches, for example, vapor-liquid-solid, vapor-solid, solution-liquid-solid, hydrothermal, template, and biomimetic methods, just name a few; however, materials that require high processing temperature, such as alkaline earth metal aluminates, are still challenging to synthesize in one-dimensional morphologies[6-10].

Barium aluminate is an efficient host material for long-lasting phosphorescence[11]. The low-temperature phase of $BaAl_2O_4$ is hexagonal, space group $P6_322$, the lattice parameters are of a= 10.449 Å and c= 8.793 Å. It has a three-dimensional network of the corner-sharing $[AlO_4]$ tetrahedra, with three-dimensionally connected open channels where the Ba^{2+} ions are located[11]. Rare earth ions with similar radius and same valence to Ba^{2+} could readily substitute for the latter with minor (if any) local distortion to the crystal lattice. This makes $BaAl_2O_4$ an ideal host material for the long-lasting phosphorescence. Synthesis and optical properties of $BaAl_2O_4$ in the form of bulk, films and nanoparticles have been exploited during the past decades[11-16]. Unfortunately, the nanoparticles with reduced dimensions generally contain high density of defects on the surface acting as radiationless recombination centers, which is detrimental to the phosphorescence properties. The successful synthesis of alkaline earth metal aluminate one-dimensional nanomaterials and nanostructures will benefit not only the study of shape-dependent phosphorescence properties, but also the fabrication of optoelectronic devices entailing guided transport of long-lasting charge carriers. However, the reports on the production of one-dimensional aluminate nanomaterials have been lingering far behind. In this work, we report on rational synthesis of single crystalline $BaAl_2O_4$ nanoplatelets by a facile hydrothermal method.

EXPERIMENTAL

In brief, $Al(NO_3)_3·9H_2O$ (4 mmol), $Ba(NO_3)_2$ (2 mmol), urea (0.01 mol), and cetyltrimethylammonium bromide (CTAB, 2mmol) were dissolved in 50 mL deionized water and stirred magnetically for 2 h. Then, the solution was poured into two Teflon-lined autoclaves with 40 mL capacity and treated in a constant temperature oven at 125 °C for 24 h. The products are washed thoroughly with ethanol and deionized water, and dried at 60 C, then annealed at 1300 °C in atmosphere for 4 h.

RESULTS AND DISCUSSIONS

The samples possessed a platelet morphology, as shown in a scanning electron microscopy (SEM) image (Figure 1a). A high-magnification SEM image in Figure 1b reveals that the nanoplatelets are well faceted, and can reach tens of micrometers in length, and the width is still in nanoscale. The transmission electron microscopy (TEM) image in Figure 1c shows clearly the nanoplatelet morphology with faceted tip. Higher magnification TEM image in Figure 1d reveals the stacking of several nanoplatelets on the wide top of one another.

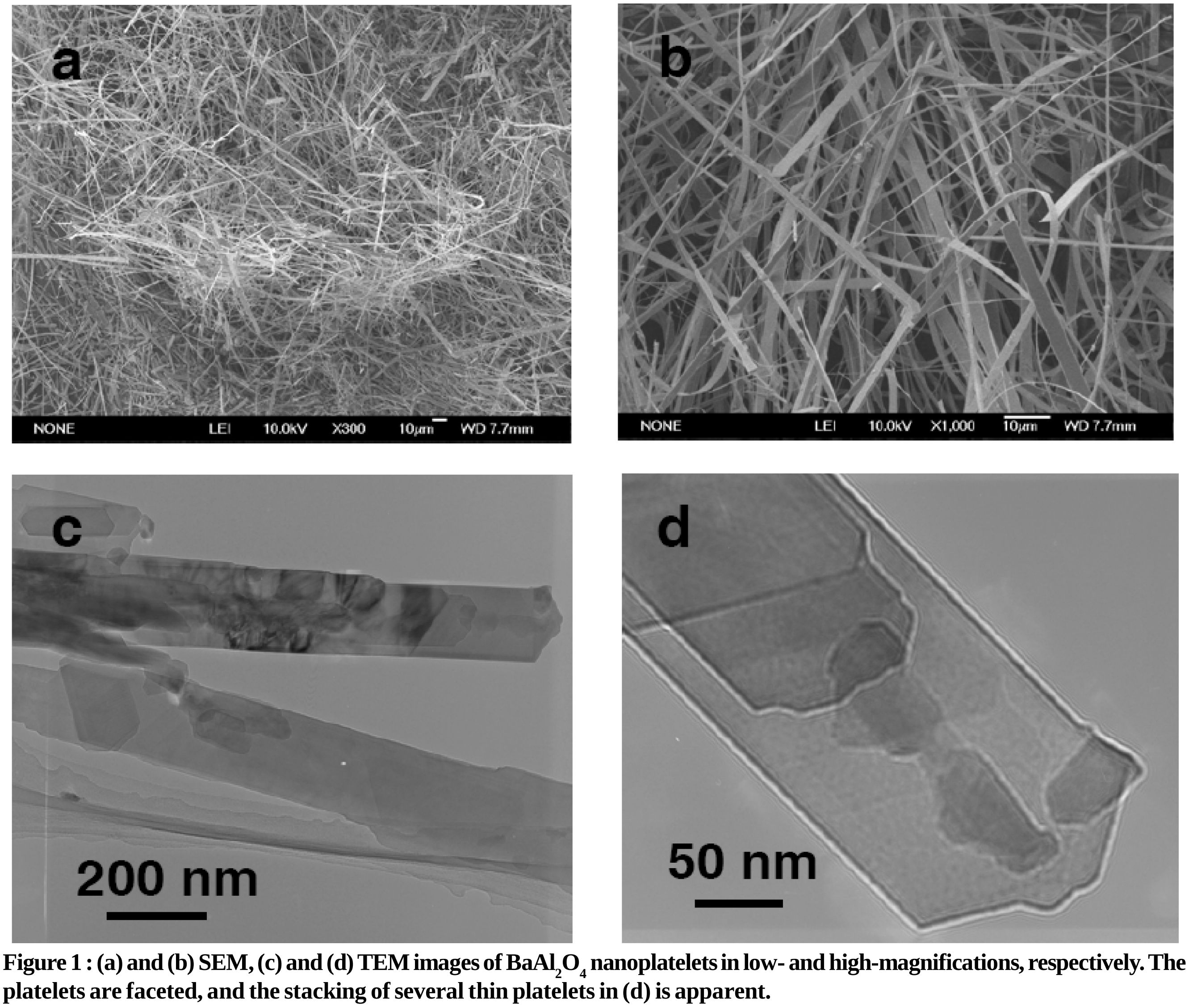

Figure 1 : (a) and (b) SEM, (c) and (d) TEM images of $BaAl_2O_4$ nanoplatelets in low- and high-magnifications, respectively. The platelets are faceted, and the stacking of several thin platelets in (d) is apparent.

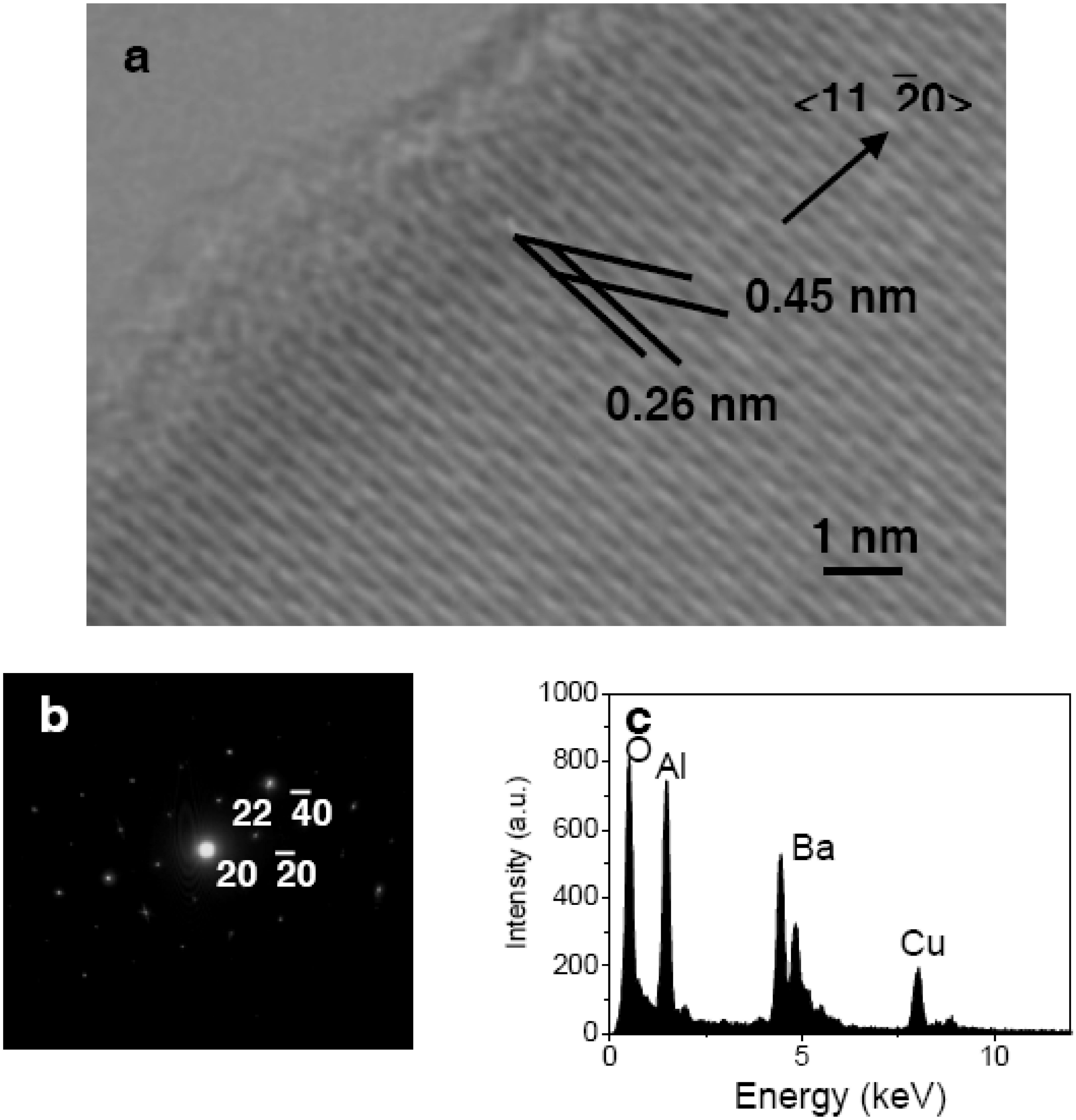

Figure 2 : (a) HRTEM image of one $BaAl_2O_4$ nanoplatelet. (b) SAED pattern of the nanoplatelet taken along the [0001] zone axis. (c) EDX spectrum of the nanoplatelet, revealing the existence of Ba, Al, and O in an atomic ratio close to 1:2:4.

To further investigate the crystal structure of the $BaAl_2O_4$ nanoplatelets, high-resolution TEM (HRTEM) attached with energy dispersive spectroscope (EDX) was employed. A HRTEM image of the edge of one $BaAl_2O_4$ nanoplatelet is exhibited in Figure 2a. The lattice fringes with spacings of 0.45 and 0.26 nm correspond to planes of $\{20\ \bar{2}0\}$ and $\{22\ \bar{4}0\}$, respectively. The growth direction of the nanoplatelet is close to $\langle 11\ \bar{2}0\rangle$. The selected area electron diffraction (SAED) pattern in Figure 2b recorded along [0001] zone axis demonstrated the single crystallinity of the nanoplatelet. The top and bottom surfaces of the nanoplatelet are ±(0001) planes. The EDX spectrum in Figure 2c reveals that the nanoplatelet is composed

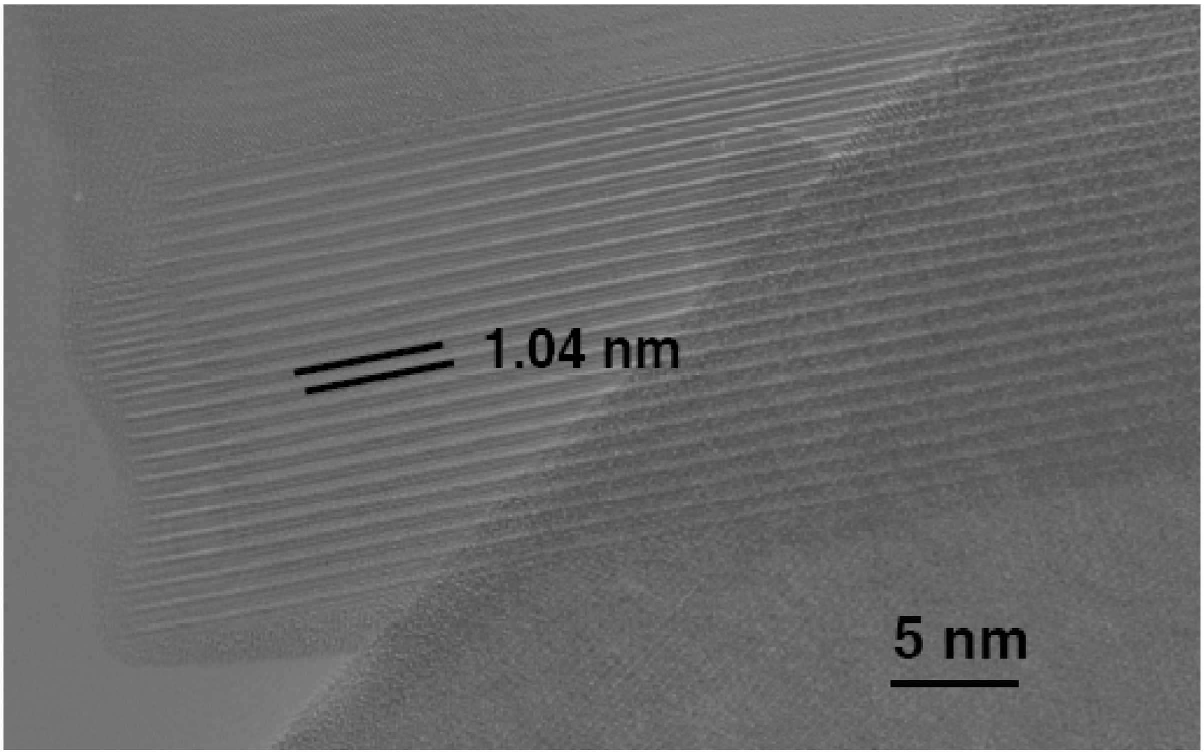

Figure 3 : HRTEM image of a $BaAl_2O_4$ nanoplatelet grown parallel to $\{2\bar{1}\bar{1}0\}$ planes.

of Ba, Al, and O elements with the atomic ratio close to the stoichiometric formula of $BaAl_2O_4$.

It is noteworthy that the growth direction of the $BaAl_2O_4$ nanoplatelets is not universal. Figure 3 shows a $BaAl_2O_4$ nanoplatelet with the growth direction parallel to $\{2\bar{1}\bar{1}0\}$ planes. The large plane spacing of the $\{2\bar{1}\bar{1}0\}$ planes (10.449 Å) make them visible even under lower magnification. As shown in Figure 4, $BaAl_2O_4$ consists of three-dimensionally linked, corner-sharing AlO_4 network. The hexagonal symmetry of this material makes its growth behavior similar to that of ZnO, with many fast growing directions[17,18].

CTAB is a well-documented reaction media allowing high ionic reactants loading and morphology modulating[19], while urea was used as a slow releasing pH adjusting agent. As demonstrated by Li *et al*[20] and Xiong *et al*[21], the positively charged CTA^+ (cetyltrimethylammonium cation) could form lamellar structures with many anionic inorganic species, especially the negatively charged oxides and hydroxides such as $[WO_4]^{2-}$, $[MnO_4]^-$, $[Ga(OH)_4]^-$, $[Zn(OH)_4]^{2-}$, and so on. The as-formed lamellar structures may not be thermally stable if they underwent high temperature annealing or chemically lost the CTA^+ groups, and then either solid nanowires or hollow nanotubes could be formed when the lamellar layer rolled up so as to reduce the stress inherent in structurally non-symmetric thin films, even though the roll-up process itself is a thermal driven process. However, if the lamellar structures are structurally symmetric (namely, the crystal structure is centro-symmetric) the driving force for the roll-up may be a little larger, and layered structure may be remained. Recently, Mallouk *et al*. demonstrated that the free energy difference between the coiled and uncoiled forms of exfoliated colloid was rather small, therefore, the appearance as rolled-up nanowires and nanotubes or unrolled layers depends on the chemical environment, such as ionic strength and pH values[22,23]. In the present work, the lamellar structures are preserved during the hydrothermal process. During the high-temperature annealing, the AlO_4 tetrahedra rearrange the organization, including the orientation and packing format to form hexagonal lattice structures. Because the rearrangement in long rang is rather energy consuming, thus, structures may be trapped at local free energy minimum, instead of overall minimum. It is, therefore, reasonable to find $BaAl_2O_4$ nanoplatelets with different growth directions and bounding surface planes.

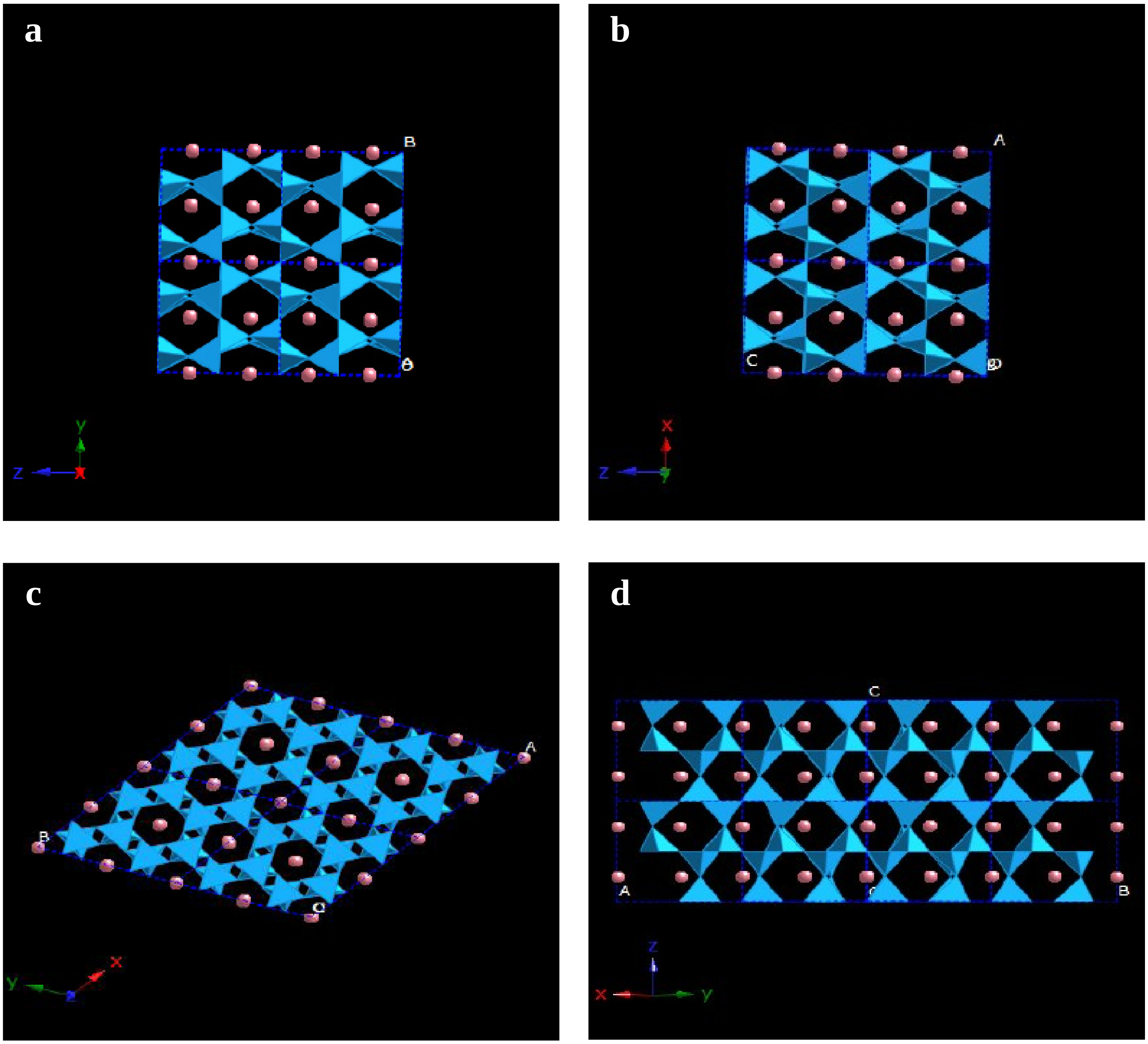

Figure 4 : Crystal structures of barium aluminate projected along different viewing directions. The corner-shared blue tetrahedra are AlO_4, and the pink colored atoms are barium.

CONCLUSIONS

In conclusion, single crystalline $BaAl_2O_4$ nanoplatelets have been synthesized by a facile hydrothermal method using CTAB as a morphology directing agent. The nanoplatelets with low density of defects and high crystallinity are ideal research targets for shape-dependent phosphorescence properties, and may also be used in long-lasting display performances. In addition, the present method is also extendable to synthesize other ternary oxide materials.

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