Organic Additive-assisted Growth of Quaternary PbX(OH) (X = Cl, Br, I) Polygonal Tubular Crystals via Ethanol Thermal Process

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Millimeter-scaled polygonal tubular crystals of PbX(OH) (X = Cl, Br, I) are successfully grown in ethanol system with the aid of polyoxyethylene *tert*-octylphenyl ether (Triton X-100). The results demonstrate that the suitable organic additive favors the growth of tubular crystals.

Recently, the syntheses of large objects (millimeter- to centimeter-scale) with open structures have been the focus of studies[1,2] because these types of structures are envisaged for potential application as ion exchanger and selective sorbets,[3] owing to their special well-defined structure, their inherent mechanical strength[4] and their ability to act as containers or capsules.[5] Existing technologies for making materials with open structures include limited stereolithography,[6] chemical processing,[7] and template-directed method[8] etc. Development of the solution routes in the mild temperature range of 100–200 °C has been motivated by current interest in the design of solid-state chalcogenides with low-dimensional structure due to the simple operation.[9] The reaction conditions applied are adequate to greatly enhance diffusion but still mild enough to keep molecular entities, such as chains and rings intact to participate in the formation of solid-state phases.[10]

In the past, laurionite-type lead halide hydroxide PbX(OH) (X = Cl, Br, I) has attracted much attention because they possessed some extraordinary structural and spectroscopic features.[11] However, there are few studies on the tubular single crystals of this series of compounds. The preparation of materials through an organic additive-mediated process is of considerable current interest, because the organic additive can alter inorganic microstructures and offer a very powerful tool for the design of new materials.[12] However, its employment is scarcely developed in the field of the preparation of single crystal in millimeter- to centimeter-scale. In this present work, three tubular prism crystals of PbX(OH) family are synthesized with the aid of Triton X-100, which is a nonionic and soluble amphiphiles. Here, hollow crystals of laurionite-type compounds grown with the assistance of Triton X-100 are first reported.

In a typical procedure, analytical grade lead acetate $PbAc_2{\cdot}3H_2O$, sodium halide NaX (X = Cl, Br, I) and Triton X-100 (molar ratio 1:2:1) were added to a Teflon-lined autoclave of 20-mL capacity with absolute ethanol up to 90% of the total volume. The autoclaves were heated at 180 °C for 72, 48, and 12 h for the preparation of PbCl(OH), PbBr(OH), and PbI(OH), respectively, and then gradually cooled to room temperature. Then the crystals obtained were washed with distilled water and ethanol successively, and dried in a vacuum at 50 °C for 5 h.

The XRD patterns[13] of PbX(OH) crystals and their polycrystalline powder, prepared by grinding the bulk crystals, are shown in Figure 1. In each XRD pattern, all the reflections can be indexed to those of the corresponding pure orthorhombic phase of PbCl(OH), PbBr(OH), and PbI(OH), respectively.[14] Figures 2b and 2d show the XRD patterns of PbCl(OH) and PbBr(OH) single crystals, respectively, in which the (110) plane of them parallels the shaft of the bulk single crystals, while Figure 2f is the XRD pattern of PbI(OH) single crystal, showing that the (101) plane of PbI(OH) crystal parallels the shaft of the bulk single crystals.

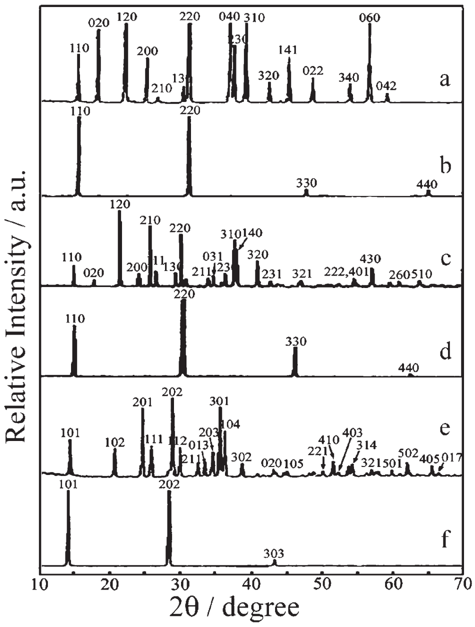

Figure 1. The XRD patterns of the products: a) powder PbCl(OH) ground from single crystals; b) single-crystal PbCl(OH); c) powder PbBr(OH) ground from single crystals; d) single-crystal PbBr(OH); e) powder PbI(OH) ground from single crystals and f) single-crystal PbI(OH).

The low magnification SEM images[13] of the PbX(OH) (X = Cl, Br, I) are shown in Figures 2a–2c, respectively, which display random distribution and fairly uniform diameter of the needle-like crystals. It can be seen that copious amounts are routinely obtained using this system. Through careful observations under high magnification (Figures 2d–2f), all the three crystals can be found to have a tubular tetragonal prismatic structure. Typically, the crystals have dimensions of ca. 10–15 mm in length, 50–70 µm in diameter, and 20–40 µm in thickness for PbCl(OH) (Figure 2d), 10–15 mm in length, 30–40 µm in diameter, and 20–30 µm in thickness for PbBr(OH) (Figure 2e), and

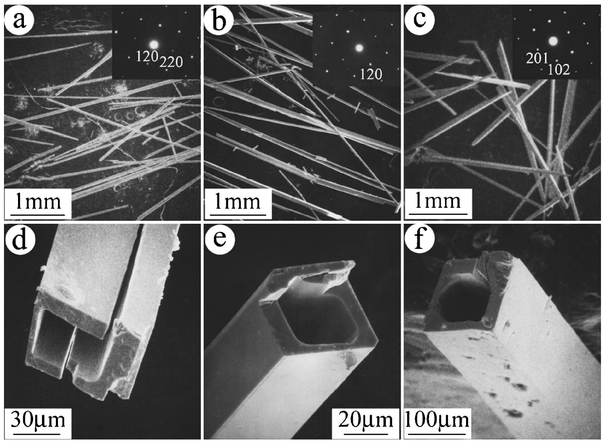

Figure 2. Low magnification SEM images of: a) PbCl(OH), b) PbBr(OH) and c) PbI(OH) single crystals and their corresponding SAED patterns (the inset); and high magnification SEM images of: d) PbCl(OH), e) PbBr(OH) and f) PbI(OH) tubular single crystals.

6–10 mm in length, 80–100 µm in diameter, and 80–100 µm in thickness for PbI(OH) (Figure 2f). The SAED patterns[13] of the as-prepared products are embedded in their corresponding low-magnification SEM images, respectively, which again confirm the feature of single crystal of these three products.

To understand the observed behavior of these three tubular crystals, it is necessary to study their structure. That is, the crystal habits of inorganic materials play an important role in the formation of the tetragonal prism structures of the laurionite-type compounds. In the following discussion, laurionite PbCl(OH) is used as an example.[11,15] The structure of the orthorhombic phase is shown in Figure 3.[15] The halogen atom is bonded to 5 Pb atoms, which form a distorted rectangular pyramid. The oxygen atom lies at the center of a tetrahedron having 3 Pb atoms and 1 hydrogen at the four vertices. Each Pb atom is linked to 5 X^- and 3 OH^- anions. The Pb-centred polyhedron may be described as a bicapped triangular prism, so in laurionite the columns of such polyhedra give rise to infinite chains running along *c* axis, by sharing Cl–Cl edges with neighbouring columns. It is understandable that the crystallite nucleates along the *c* axis and grows readily because of the inherent chain type structure, which makes the need-like morphology form. As to the formation of hollow tubular, it could be attributed to the difference in the adsorption effect of Triton X-100 on the different faces of PbX(OH) crystals, which maybe results in the formation of hollow interior, because in the controlled experiments the hollow tubular structures cannot be obtained in the absence of Triton X-100. On the other hand, the sealed reaction system can provide an unstable and nonequilibrium experimental conditions, including the high reaction temperature and high reaction pressure, which may be propitious to the growth of the PbX(OH) tubular crystals.[9] However, the detailed mechanism is not fully understood and needs to be further studied.

In summary, a feasible organic additive-assisted method is successfully developed to grow the lead halides hydroxide tetragonal prismatic tubular crystals in millimeter-scale by a mild ethanol thermal process. The experimental results demonstrate that the organic additives used can direct the growth of crystals with definite shape, which enlightens us that the morphology of the materials can be controlled by using suitable organic additive.

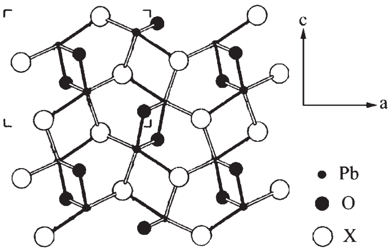

Figure 3. The crystal structure of laurionite-type compounds as seen along [010]. Hydrogen atoms are not indicated. The unit cell limits are outlined. Empty sticks denote a single interatomic bond between atoms at the same level, whereas filled sticks denote double bonds with two atoms lying on opposite neighbouring planes.

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13 XRD patterns were taken on a Japan Rigaku D/max rA X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation source ($\lambda = 1.54178$ Å) and employing a scanning rate of $0.06^\circ \cdot s^{-1}$ in the 2θ range of 10–70°. Scanning electronic microscopy (SEM) images were taken by an X-650 scanning electron microanalyzer. Selective area electronic diffraction (SAED) patterns were recorded on a Hitachi Model H-800 using an accelerating voltage of 200 kV.
14 JCPDS Card Files No. 31-680 for PbCl(OH), No. 30-697 for PbBr(OH) and No. 22-655 for PbI(OH).
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