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Synthesis of new complex salt crystal $K_3[InCl_6]$

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Abstract During the experiment of preparing ITO (Indium Tin Oxide) nanopowder, a new complex salt crystal $K_3[InCl_6]$ was found and synthesized using a solution growth method. The diffraction pattern, morphology, element composition and structure of the crystal were analyzed by XRD, SEM and CCD. The results implied that $K_3[InCl_6]$ is monoclinic, is of the space group $P2_1/c$, has a chemical formula of $K_3[InCl_6]$, a $Z = 4$ and with the following cell parameters: $a = 12.188 \text{ \AA}$, $b = 7.553 \text{ \AA}$, $c = 12.703 \text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 108.96^\circ$, $\gamma = 90.00^\circ$, $V = 1105.98 \text{ \AA}^3$.

Keywords $K_3[InCl_6]$, crystal structure

1 Introduction

Precipitation method is one of the main ways to prepare Indium-Tin-Oxide (ITO) nanopowders. There were many reports about the preparation of ITO nanopowders by precipitation method [1–4], but none about the formation and influence of complex ions during the preparation of ITO nanopowders, until now. A new complex salt crystal, $K_3[InCl_6]$ was found and synthesized by using a solution growth method during the experiment of preparing ITO nanopowders by the complex salt hydrolysis co-precipitation method.

2 Synthesis and test of crystal

The title compound was synthesized by the solvent evaporation method. The reaction solution was prepared by

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mixing $In(OH)_3$, K_2CO_3 and hydrochloric acid in the molar ratio of $n(In(OH)_3):n(K_2CO_3):n(HCl) = 2:3:12$. Colorless transparent crystals were obtained by drying the reaction solution in a constant-temperature oven at 323 K for several days. The diffraction pattern of the crystal was characterized by a D8-Advance X-ray diffractometer made in Germany by the Bruker Company. The crystal morphology and element composition were analyzed by a JSM-5610LV made by JEOL Ltd.. The crystal structure was characterized by SMART APEX-CCD X-ray diffractometer made by the Bruker Company, Germany.

3 Results and discussion

3.1 Control of the crystal growth condition

The reaction solution was prepared by mixing $In(OH)_3$, K_2CO_3 and hydrochloric acid in the molar ratio of $n(In(OH)_3):n(K_2CO_3):n(HCl) = 2:3:12$. A colorless transparent crystal was obtained by drying the reaction solution in a constant temperature oven. The crystal is sensitive to moisture in the air. The size of crystal precipitated from solution was tiny and the shape was indistinct when the drying temperature was $80^\circ C$. However, when the drying temperature went down to $50^\circ C$, its size grew and it could be distinguished more clearly. Figure 2 shows the crystal with a transparent and thick plate. When the drying temperature was low, the ionic supersaturation degree and quantity of crystal nuclei to form crystals were low. The supersaturation degree was slowly decreased and the crystal growth speed was comparatively fast. On the other hand, the time of crystal growth was greater at lower temperatures. The crystals precipitated from the solution grew well and the grain size was large.

The prohibition of KCl crystallization from solution was the most difficult procedure to be controlled. Figure 1(a) shows the XRD of crystals which crystallized from the solution mixed by $n(In(OH)_3):n(K_2CO_3):n(HCl) = 2:3:12$ (mole ratio) at $50^\circ C$. KCl crystals were in great quantities from XRD analysis. During the solution's drying procedure, the amount of In^{3+} was reduced

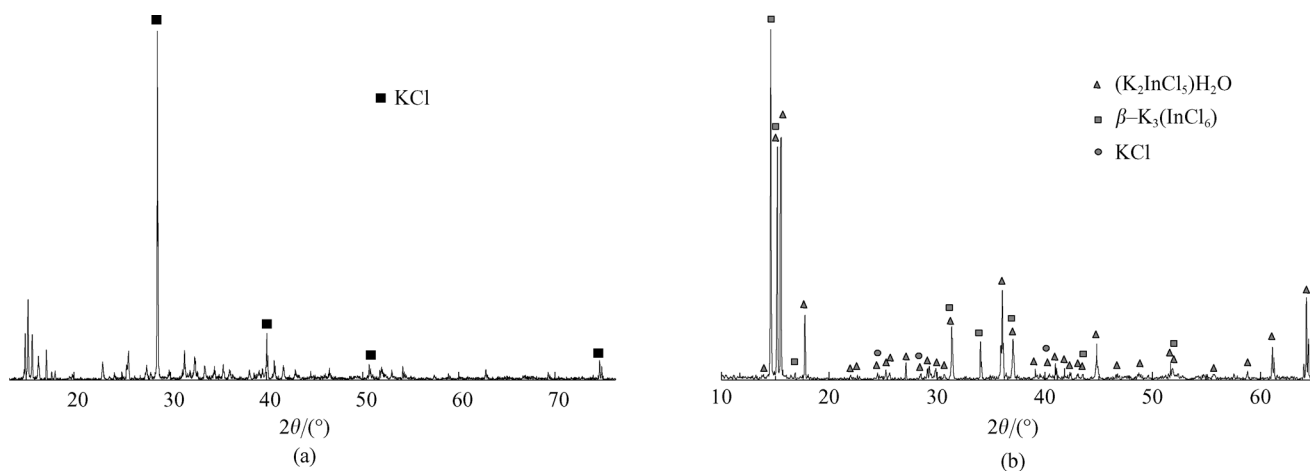


Fig. 1 XRD of synthesized crystal at different K_2CO_3 quantity
(a) K_2CO_3 quantity = theoretic value; (b) K_2CO_3 quantity = 75% of theoretic value

because of the evaporation at $50^\circ C$. The element ratio was no longer stoichiometric and KCl was crystallized from the solution first, which helps by causing more KCl to be crystallized. That is why KCl is the main product. To lower the effect of $InCl_3$ evaporation, the K_2CO_3 dosage was decreased. Figure 1(b) shows the XRD of crystals synthesized from the solution in which K_2CO_3 dosage was cut down to 75% of the stoichiometric dosage at $50^\circ C$. It was observed from Fig. 1(b) that the content of KCl lessened. From Comparing Fig. 1(b) to PDF (840190), it was supposed that the crystal was $K_2InCl_5 \cdot H_2O$. But the $K_2InCl_5 \cdot H_2O$ was an orthorhombic system, and the shape of an orthorhombic crystal would never be as thick as the one which was shown in Fig. 2. So the crystal might be a new crystal or an isomeride of $K_2InCl_5 \cdot H_2O$.

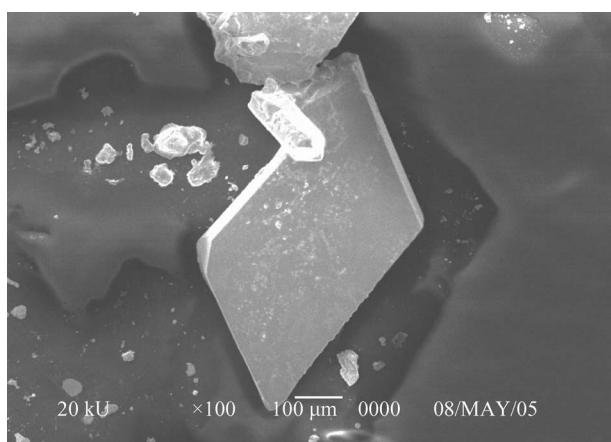


Fig. 2 Picture of crystal $K_3[InCl_6]$

3.2 Crystal composition analysis

The chemical composition of thick-board crystal in Fig. 2 was analyzed by EDS attached to JSM-5610LV SEM

produced by JEOL Ltd. Figure 3 was its energy spectrum. Elements K, Cl and In could be seen. The first peak in spectrum belonged to element B which was due to a systematic error. Figure 4 was the element surface distribution of the crystal. The upper-left element was Cl. The upper-right element was K and the lower-left element was In. The three elements were distributed evenly and neither a dense

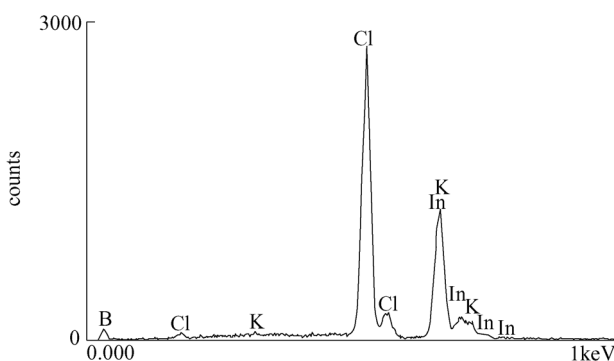


Fig. 3 Energy spectrum of $K_3[InCl_6]$

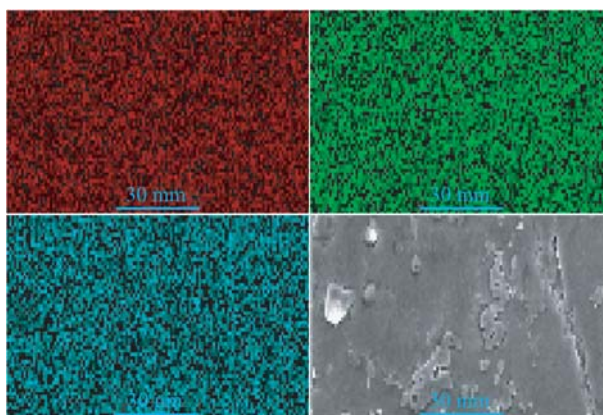


Fig. 4 Facial scanning picture of $K_3[InCl_6]$

nor a sparse area of the elements was found. It indicated that the crystal was composed of K, In and Cl.

3.3 Single crystal structure analysis

The appropriate single crystal picked out by microscope (the grain size was $0.28\text{ mm} \times 0.50\text{ mm} \times 0.09\text{ mm}$) was analyzed by CCD X-ray diffractometer produced by Bruker. The results indicated that $K_3[InCl_6]$ is monoclinic, with space group $P2_1/c$, a chemical formula of $K_3[InCl_6]$, a $Z = 4$ and cell parameters of $a = 12.188\text{ \AA}$, $b = 7.553\text{ \AA}$, $c = 12.703\text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 108.96^\circ$, $\gamma = 90.00^\circ$, $V = 1105.98\text{ \AA}^3$. Figure 5 is the $K_3[InCl_6]$ cell structure model according to the results calculated by CCD X-ray diffractometer. In^{3+} which has six coordinates, filled in the octahedral interstice constructed by Cl^- to form an $[InCl_6]^{3-}$ complex anion. $[InCl_6]^{3-}$ complex anions are located at the center each of the edges of the cell and in the center of the cell. K^+ took the interstices constructed by $[InCl_6]^{3-}$ complex anions. There were 4 In^{3+} , 24 Cl^- and 12 K^+ in every cell.

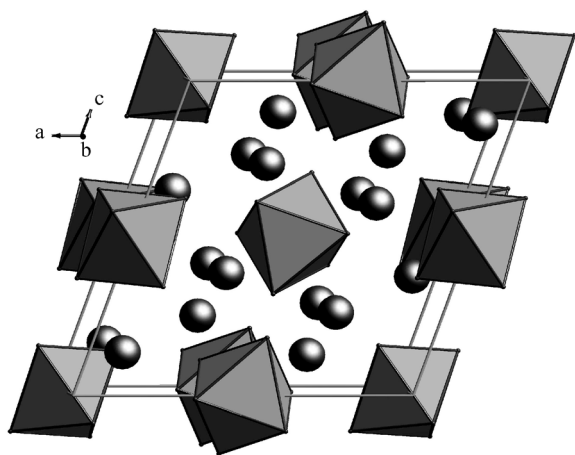


Fig. 5 $K_3[InCl_6]$ crystal cell structure model

Four PDF cards about K_3InCl_6 (21-0647, 21-0648, 34-0307 and 34-0308 respectively) which belonged to

tetragonal system were reported till now. No monoclinic K_3InCl_6 was reported. The crystal was testified as a new one because its XRD was not consistent with those which have been found along with the analytic element

4 Conclusions

A new complex salt crystal, $K_3[InCl_6]$ was found and synthesized using a solution growth method during the experiment of preparing ITO nanopowders by the complex salt hydrolysis co-precipitation method. The crystal structure was characterized by SMART APEX-CCD X-ray diffractometer, the results indicating that $K_3[InCl_6]$ is monoclinic, with a space group $P2_1/c$, chemical formula of $K_3[InCl_6]$, $Z = 4$, cell parameters $a = 12.188\text{ \AA}$, $b = 7.553\text{ \AA}$, $c = 12.703\text{ \AA}$, $\alpha = 90.00^\circ$, $\beta = 108.96^\circ$, $\gamma = 90.00^\circ$, $V = 1105.98\text{ \AA}^3$. The XRD of K_3InCl_6 crystal which was synthesized by us was not consistent with those which had been reported. Through element analysis, the crystal was testified as a new one, but its properties and usage have to be studied further.

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