Preparation of ATO Nanoparticles from a New Composite Complex Salt

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A new composite complex salt—\((\text{NH}_4)_1.8(\text{Sn}_{0.9}\text{Sb}_{0.2})\text{Cl}_6\) was synthesized at room temperature from the starting materials \(\text{SnCl}_2\)-5\(\text{H}_2\text{O}\) and \(\text{SbCl}_3\). Its XRD pattern was indexed. The ATO nanoparticles were then obtained by sintering the composite complex salt at various temperatures. Analyses revealed the obtained ATO nanoparticles are single phase belonging to tetrahedral rutile structure.

1. Introduction

As one kind of potential semi-conductive materials, Antimony doped tin oxide (ATO) has obvious advantages compared to traditional conductive materials in light transparency, mechanical and environmental stabilities, dispersibility and multifunction.1) With the development of LCD (liquid crystal display), ATO is highly demanded. As the transparency, mechanical and environmental stabilities, dispersibility and multifunction.

Recently, general way to prepare ATO is mixing \(\text{SnCl}_2\)-5\(\text{H}_2\text{O}\) and \(\text{SbCl}_3\) in HCl dense solution, and thus the precursors were produced by coprecipitation method. After washing, drying and heat treatment procedures, ATO nanoparticles were obtained.2–4) This method is very simple but has some problems. That is, the existed Cl\(^-\) not only makes precipitate washing difficult, but also decreases the conductivity of powder and increases the number of non-bridge formation –OH, which severely affects the dispersibility of powder particles. If this method is applied to practical production, Cl\(^-\) will also corrupt electronic equipments. Therefore, it is meaningful to study new way to produce ATO nanoparticles.

In this paper, ATO powder was prepared from a new composite complex salt—\((\text{NH}_4)_1.8(\text{Sn}_{0.9}\text{Sb}_{0.2})\text{Cl}_6\) which was synthesized from the starting materials \(\text{SnCl}_2\)-5\(\text{H}_2\text{O}\), \(\text{SbCl}_3\) and Ammoniac salt. Then it was sintered at certain temperature, and conductive carriers formed due to a lot of vacancy defects when solid-phase reaction happened. Finally, excellent ATO conductive powders were prepared.

2. Experimental

The solutions A was prepared by mixing \(\text{SbCl}_3\) and absolute ethanol at room temperature, the solutions B was the mixed solutions of \(\text{SnCl}_2\)-5\(\text{H}_2\text{O}\) and absolute ethanol, then mixed A and B at molar ratio of \(\text{Sb}_2\text{O}_3 : \text{SnO}_2 = 1 : 9\). Ammoniac salt solution (10%) was added to the solution to precipitate the \(\text{Sn}^{4+}\) and \(\text{Sb}^{3+}\) ions until certain pH value was reached 4. After 30 minutes on standing, the solution was dried at 80\(\degree\)C. Finally, yellow octahedron crystal was prepared. Then the crystal was dissolved in distilled water followed by grounding, ammoniac salt solution was dropped into it to adjust pH value. Hereafter, the resulting canary precipitate was washed with distilled water and absolute ethanol for 3 times, respectively, and then dried at 80\(\degree\)C. ATO powders were prepared by sintering the precipitate in muffle furnace in reducing atmosphere.

Phase analysis was characterized by X-ray diffraction (model RigaKu D/MAX 2500V, Japan, \(\lambda = 0.15406\) nm). The morphology of the canary octahedron crystal was observed with Scanning Electron Microscopy (SEM, model SX-40, Japan). The average grain size of the prepared ATO particle was calculated from the Scherrer’s formula \(D = k\lambda/\beta\cos\theta\), where \(\lambda\) is the wavelength of X-rays, \(\beta\) is the corrected half-width.

3. Results and Discussion

Figure 1 shows the XRD patterns of the synthesized crystal. All peak positions agree well with the reflections of bulk cubic \((\text{NH}_4)_2\text{SnCl}_6\) (JCPDS 07-0198). No other adulterants are added in the production procedure. The obtained crystal with regular octahedron structure is yellow and transparent which is different from transparent \((\text{NH}_4)_2\text{SnCl}_6\). Therefore the crystal must be a new compound. Because the radius of \(\text{Sb}^{3+}\) is larger than that of \(\text{Sn}^{4+}\), doping antimony results in the crystal cell of \((\text{NH}_4)_2\text{SnCl}_6\) swelling and crystal lattice distorting, transforming and loosening. Then cell...
The parameters of \((\text{NH}_4)_2\text{SnCl}_6\) changed along with the elastic distortion of crystal lattice happening. Its structure analysis is listed in Table 1.

Figure 2 shows the morphology of \((\text{NH}_4)_2\text{SnCl}_6\) powders. It is obvious that \((\text{NH}_4)_2\text{SnCl}_6\) belongs to octahedral structure crystal, edge angles are many and distinct, and grain size is homogeneous.

Figure 3 shows the XRD patterns of ATO powder at different temperatures. In all cases, the peak positions agree distinctly, and grain size is homogeneous.

Table 1: Structure analysis of \((\text{NH}_4)_1.8(\text{SnO}_2\text{Sb}_0.2)\text{Cl}_6\).

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Table 1: Structure analysis of \((\text{NH}_4)_1.8(\text{SnO}_2\text{Sb}_0.2)\text{Cl}_6\).

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

in which \(k = 0.9\), \(\lambda = 0.15\) nm (CuK\(\alpha_1\)).

The size increased from 13.2 nm at 300°C to 64.3 nm at 500°C and 70.4 nm at 600°C, respectively, which witnessed the growth of the nanoparticles. The crystal size grew slowly at low temperature, and increased quickly with the increase of sintering temperature. But it became stable after 600°C.

Crystal phase of ATO is \((\text{SnO}_2\text{Sb}_0.2)\text{Cl}_6\). See from the figure of SnO\(_2\) crystal structure (Fig. 4), Sn\(^{4+}\) lies in one second place of octahedral void, which is 6-fold-coordination, and O\(^{2-}\) could be approximately considered as hexagonal closet packing. It is well known that oxidation state of Sb\(^{3+}\) is prone to change at high temperature, its high activity would let it enter SnO\(_2\) crystal lattice to replace Sn\(^{4+}\) or take up unoccupied octahedral void to form substitutional or interstitial solid solution. The different radius between Sn\(^{4+}\) and Sb\(^{3+}\) results in SnO\(_2\) crystal lattice distortion when Sb\(^{3+}\) replace Sn\(^{4+}\). Sb\(^{3+}\) lying in octahedron is in bondage to top atom, so its electron cloud is transformed, leading to visible light reflected strongly in one certain range and decreased gradually in another certain range, therefore, the color of crystal is blue. With the increasing of heat treatment temperature, more doped Sb\(^{3+}\) in SnO\(_2\) crystal lattice which make electrons in donor energy level prone to be triggered, add up to the effect of quantum dimension, The color change dark.
4. Conclusion

A new compound—\((\text{NH}_4)_1.8(\text{Sn}_{0.9}\text{Sb}_{0.2})\text{Cl}_6\) was found for the first time. And its XRD pattern was indexed. ATO has been prepared successfully through sintering the new compound.

The prepared ATO is rutile structure. Powder size is influenced by heat treatment temperature greatly. The size of particles sintered at low temperature (300°C, 400°C) was about 10 nm, while sintered at high temperature is above 60 nm.

Color of ATO is azury due to doped Sb introducing donor energy level. Because of the increase of concentration of carriers and quantum dimension effect, samples under high heat treatment temperature showed different blueness.

Acknowledgment

This work was mainly supported by Guangxi Academic Degrees Committee 2003 Degree Authorizations Office Academic Construction Fun, and State Key Lab of Advanced Technology for Materials Synthesis and Processing of Wuhan University of Technology.

REFERENCES