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Preparation of ATO Nanoparticles from a New Composite Complex Salt

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A new composite complex salt—$(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$ was synthesized at room temperature from the starting materials $SnCl_4{\cdot}5H_2O$ and $SbCl_3$. 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.
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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 purity and fineness of the oxide powder increased, the high performance products may be easily obtained.

Recently, general way to prepare ATO is mixing $SnCl_4{\cdot}5H_2O$ and $SbCl_3$ 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\underline way to produce ATO nanoparticles.

In this paper, ATO powder was prepared from a new composite complex salt—$(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$, which was synthesized from the starting materials $SnCl_4{\cdot}5H_2O$, $SbCl_3$ 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 $SbCl_3$ and absolute ethanol at room temperature, the solutions B was the mixed solutions of $SnCl_4{\cdot}5H_2O$ and absolute ethanol, then mixed A and B at molar ratio of $Sb_2O_3 : SnO_2 = 1 : 9$. Ammoniac salt solution (10%) was added to the solution to prepcipitate the Sn^{4+} and Sb^{3+} ions until certain pH value was reached 4. After 30 minutes on standing, the solution was dried at 80°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°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 λ is the wavelength of X-rays, β 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 $(NH_4)_2SnCl_6$ (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 $(NH_4)_2SnCl_6$. Therefore the crystal must be a new compound. Because the radius of Sb^{3+} is larger than that of Sn^{4+}, doping antimony results in the crystal cell of $(NH_4)_2SnCl_6$ swelling and crystal lattice distorting, transforming and loosening. Then cell

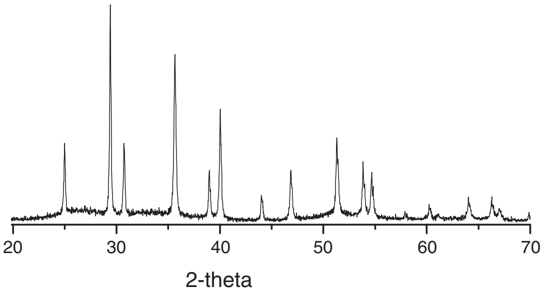

Fig. 1 XRD patterns of $(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$.

Table 1 Structure analysis of $(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$.

#	*d*	*I*/*I*0	hkl	#	*d*	*I*/*I*0	hkl
1	5.8236	100	111	10	1.9379	16.9	511
2	5.0405	63.5	200	11	1.7795	27.4	440
3	3.5619	16.7	220	12	1.7014	15.7	531
4	3.0358	45.9	311	13	1.6773	12.4	600
5	2.9078	17.8	222	14	1.5918	2.1	620
6	2.5170	53.9	400	15	1.5354	3.7	533
7	2.3091	11.6	331	16	1.4531	8.7	444
8	2.2502	32.3	420	17	1.4091	5.3	711
9	2.0561	6.6	422	18	1.3959	3.0	640

sys: Cubic S.G.: Fm3m(225) $a = 1.0087\,\text{nm}$

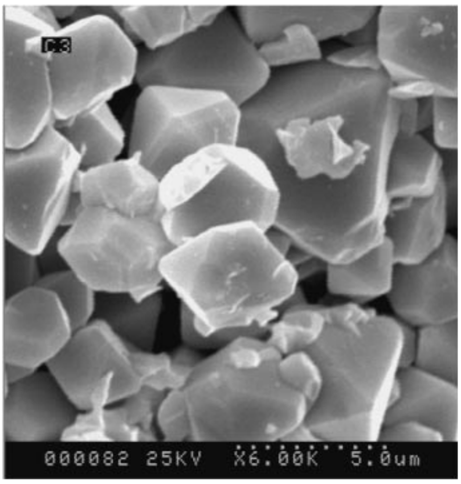

Fig. 2 SEM of $(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$.

parameters of $(NH_4)_2SnCl_6$ changed along with the elastic distortion of crystal lattice happening. Its structure analysis is listed in Table 1.

Figure 2 shows the morphology of $(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$. It is obvious that $(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$ 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 well with the reflections of bulk cassiterite SnO_2 (JCPDS 21-1250), the structure of the prepared ATO powder is regular tetrahedral rutile structure. Antimony doping only make peak positions shift a little, no other phases were detected. It is indicated that all antimony ions come into the crystal lattice of bulk SnO_2 to substitute for tin ions, and ATO prepared by the new composite complex salt is completely applicable. The XRD diffraction lines are broadened when powders are sintered at lower than 500°C, indicating nanosized crystallites in the samples. The width decreases with the increase of sintering temperature, indicating growth of nanosized crystallites and integrity of cell structure.

The average crystallite sizes of ATO nanoparticles determined from the (110) plane by the Scherrer's formula were listed in Table 2.

$$D = k\lambda/\beta \cos\theta$$

in which $k = 0.9$, $\lambda = 0.15\,\text{nm}$ ($\text{CuK}\alpha_1$).

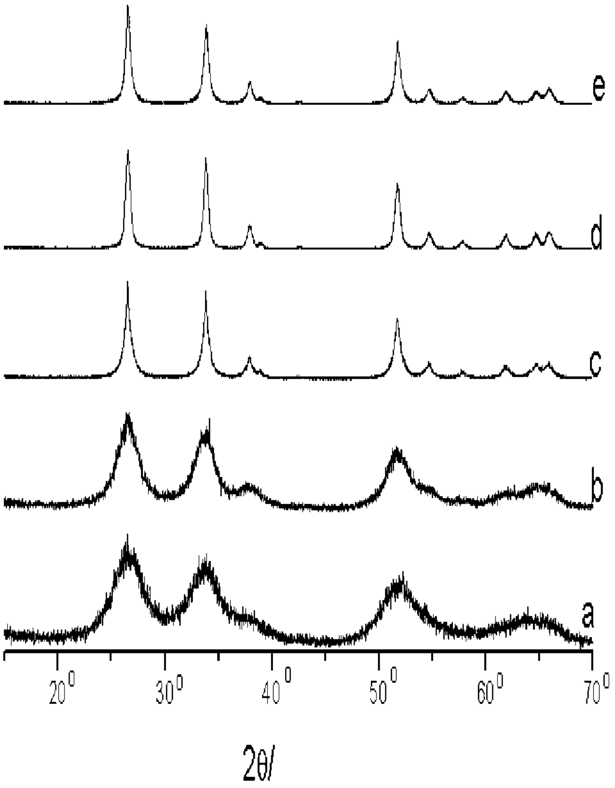

Fig. 3 XRD patterns of ATO at different temperatures. a: 300°C; b: 400°C; c: 500°C; d: 600°C; e: 700°C.

Table 2 Relationship between sintering temperature and crystallite size.

Sintering temperature [*T*/°C]	300	400	500	600	700
Grain diameter [*d*/nm]	13.2	14.6	64.3	70.4	72.8

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 $(Sn_{0.9}Sb_{0.2})O_{2.1}$, belonging to cassiterite SnO_2. 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+}, resulting in SnO_2 crystal lattice distortion when Sb^{3+} replace Sn^{4+}. Sb^{3+} lieing in octahedron is in bondage to top atom, so its electron cloud is transformed, leading to visible light reflected stronged in one certain range and decreased gradually in nother 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.

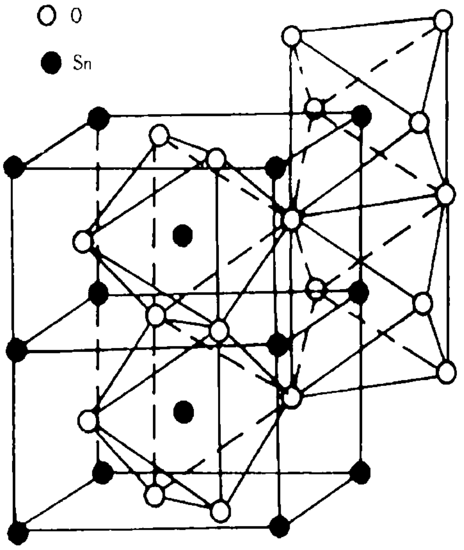

Fig. 4 SnO_2 crystal structure.

4. Conclusion

A new compound—$(NH_4)_{1.8}(Sn_{0.9}Sb_{0.2})Cl_6$ 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.

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REFERENCES

1) J. Rockenberger, V. Zum Felde and M. J. Tischer: Chem. Phys. **112** (2000) 4296–4304.
2) C. Goebbert, H. Bisht, N. A. Dahoudi, R. Nonninger, M. A. Aegerter and H. Schmidt: J. Sol-gel Sci. Technol. **19** (2000) 201–204.
3) C. Marcel and M. S. Hegde: Electrochimica Acta. **46** (2001) 2097–2104.
4) J. P. Coleman, J. J. Freeman, A. Rougier, P. Madhukar and J. H. Wagenknecht: Displays. **20** (1999) 145–154.