Study on the Key Technology of High Purity Strontium Titanate Powder Synthesized from Oxalic Acid Co-sediment Precipitation

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Abstract. Oxalate coprecipitation is applied in this paper, high purity titanium tetrachloride, and after the purification of strontium chloride, match with a certain concentration of solution, oxalate and strontium chloride and titanium tetrachloride in 1.005:1.000 make strontium titanium mixture ratio, slowly under 60 ℃ to join in oxalic acid solution, aging around 4 h, get oxygen titanium strontium oxalate \( \text{SrTiO(C}_2\text{O}_4)_2 \cdot 4\text{H}_2\text{O} \) precipitation, after washing, drying and other process made oxygen titanium strontium oxalate powder.

1. Introduction

Oxygen titanium strontium oxalate as the preparation of strontium titanate lead reactants, and strontium titanate is an important raw material, the electronics industry to automatically adjust the heating element and manufacturing have demagnetizing effect of components. In the field of ceramics for making ceramic capacitors, sensitive piezoelectric ceramic materials, ceramic components, microwave ceramic components, so the study of the preparation of high purity titanium strontium oxalate oxygen has the necessity.[1-3]

In this paper the research of high purity titanium strontium oxalate oxygen is used in the preparation of strontium titanate optical single crystal, due to the preparation of titanium optical grade strontium single crystal of the purity of titanium strontium oxalate oxygen, strontium titanium ratio and is very tall to the requirement of chemical homogeneity, the experiment research of chemical coprecipitation preparation powder of high purity, uniform particle size distribution, specific surface area is big, good for doping raw material components in the mixture, reaction is in highly fragmented state of atomic, molecular, uniform product reaction, thorough and consistent structure, which can obtain high quality of high stability good oxalic acid strontium titanium powder, oxygen in liquid phase reaction, easy to control the molar ratio of titanium strontium, simple equipment, process, compact construction, low cost and is beneficial to industrialized production, so choose oxalate coprecipitation preparation of strontium titanate optical single crystal get satisfy oxygen titanium strontium oxalate powder.

2. Experiment

The chemical reagents such as strontium chloride, four titanium chloride, oxalic acid, ethanol and so on were used in this experiment. The experimental process is shown in figure 1. SEM images using SUPRATM 55 (Carl Zeiss AG) uptake.
3. Results and discussion

3.1. Preparation of four titanium chloride aqueous solution

Under normal temperature, TiCl$_4$ and water contact reaction, the formation of a large volume of yellow precipitate or white precipitate, and release a lot of reaction heat. The yellow precipitate is soluble in the hydrochloric acid solution generated by the reaction of TiCl$_4$ with water to form TiCl$_4$ hydrochloric acid aqueous solution (TiCl$_4$ solution). In fact, the reaction process between TiCl$_4$ and water is very complex, which is related to the concentration of titanium ion, solution temperature and solution acidity. When they begin to contact, they form hydrates. If the water is sufficient, the five (TiCl$_4$ •5H$_2$O) is preferentially formed, while the water content is low and the low temperature, the formation of a compound of water (TiCl$_4$ •2H$_2$O). Then the hydrate is hydrolyzed. In the process of hydrolysis, the chlorine atoms in TiCl$_4$ are gradually replaced by OH$^-$ groups, and HCl and Ti(OH)$_n$Cl$_{4-n}$ (n =1,2,3,4) type compounds are formed. The reaction process is rapid at high temperature, the reaction is slow at low temperature, and the intermediate product can be precipitated; When the water is insufficient, the hydrolysis process can stay in an intermediate stage; When the water is excessive, the hydrolysis process of TiCl$_4$ can be carried out in the end. After a long period of time (aging) or heating, the titanic acid can be converted into a more stable H$_2$TiO$_3$ [4,5] Four titanium chloride (TiCl$_4$) in water for TiOCl$_2$, directly into the ice TiCl$_4$ inside, it is best to fall on the ice cube, can also be slowly dropped into the ice water mixture, the water temperature should not exceed five degrees celsius. Four titanium chloride water solution preparation of the two key indicators, one is the feeding speed, the temperature is two feeding process, because four titanium chloride easily hydrolyzed into titanium dioxide (white precipitate), making the final preparation of strontium strontium titanate powder, titanium ratio deviation to obtain high purity strontium titanate powder.

In this study, three methods were used to inhibit the hydrolysis of titanium chloride and finally to obtain a colorless and transparent solution of titanium chloride. A: for four titanium chloride placed in the freezer to reduce its temperature; two: manufacturing low temperature electric oven, oven dry ice can be added to (or nitrogen) to reduce the temperature and humidity in the constant temperature box; three: four titanium chloride is slowly added into ice water mixture with deionized water or dry ice. And continue to join the ice in the process of dropping, in order to avoid the temperature to four titanium chloride hydrolysis degree becomes larger.

Figure 1. Flow chart of strontium titanate powder preparation.
3.2. Effect of raw material purification
The recrystallization and purification of strontium chloride and oxalic acid were carried out. In order to study the influence of the purity of the reactants on strontium titanate powder, we set up two sets of control experiments to obtain the strontium titanate powder under the condition of flame fusion crystal growth. The results are listed in table 1.

| Whether purification | T (°C) | Time (hours) | Productivity (g) | Theoretical strontium titanium ratio | Crystal case               |
|----------------------|--------|--------------|------------------|-------------------------------------|---------------------------|
| 1 No                 | 60     | 4            | 83.541           | 1.005:1.000                        | Features are not clear    |
| 2 Yes                | 60     | 4            | 92.515           | 1.005:1.000                        | Cracks clear and transparent |

The purification of oxalic acid and strontium chloride, strontium titanate powder particles are not uniform, poor mobility, and the calcined crystal appearance is not clear, the crack growth, the initial judgment is by the impurity in the reactants (iron or lead, barium ion) for purification after the normal production, powder uniform particle size, crystal clear appearance, improved transparency.

3.3. Effect of temperature and time on the coprecipitation of oxalic acid
We are at 55 degrees Celsius, 60 degrees Celsius, 70 degrees Celsius under the condition of keeping strontium and titanium than 1.000:1.000, precipitation time of 4 hours, postprocessing calcination temperature of 900 degrees Celsius conditions unchanged comparing experiment, crystal growth and characterization of SEM results in table 2. Under the condition of 55 degrees Celsius, the yield of strontium titanate is obviously low, which indicates that the precipitation is not complete. From the point of view of the crystal, 55 degrees Celsius and 70 degrees Celsius under the conditions of the powder containing different melting point substances (impurities), can not see the crystal when calcined. 60 degrees Celsius to get better powder growth.

| T (°C) | Productivity (g) | Crystal growth                  | Average particle size (μm) |
|--------|-------------------|---------------------------------|-----------------------------|
| 1      | 55                | 94.745                          | Material with different     |
|        |                   |                                 | melting point               | 3.23                        |
| 2      | 60                | 135.039                         | preferably                  | 3.24                        |
| 3      | 70                | 124.727                         | Material with different     |
|        |                   |                                 | melting point               | 7.62                        |

By scanning SEM on the morphology of strontium oxalate powders (Figure 2 and 3), we find that with the increase of temperature, strontium titanyl oxalate particles changes exponentially, at 40 degrees Celsius to 60 degrees Celsius, the crystal grain size changes slowly, when the temperature exceeds 60 degrees Celsius when the growth of crystal particle size quickly. Synthetic temperature on the crystal size effect is significant, the analysis result is: when the reaction temperature is low, the solubility of strontium titanyl oxalate crystal nucleus is very small, relatively easy to precipitate, but not conducive to the growth of the crystal nucleus, so the crystal size is smaller. With the increase of temperature rise, the solubility of strontium titanyl oxalate, nucleation precipitation is relatively difficult, but is conducive to the growth of the crystal nucleus, so the crystal size is larger, can be seen from the figure at 60 degrees Celsius temperature of the crystal size has increased significantly, from many aspects to consider to determine whether 60 degrees Celsius the best synthesis temperature centigrade.
Figure 2. Scanning electron microscopy (SEM) of strontium oxalate powder

Figure 3. Relationship between temperature and particle size

At the same time, the results showed that the yield and properties of the obtained powders were not significantly different when the co precipitation reaction time was more than 4 hours, indicating that the precipitation was sufficient, and the total precipitation time was selected for 4 hours.

3.4. Effect of calcination temperature and time on the oxidation of strontium oxalate

The calcination process is the thermal decomposition process of strontium oxalate, and the calcination temperature is directly related to the thermal decomposition of the reactants. If the calcining temperature is too low or the time is too short, the decomposition will be incomplete, and the diffusion of strontium and titanium will be uneven. When the calcination temperature is too high, the particle size of strontium titanate powder will become larger, resulting in sintering. To get the optimum calcination temperature, strontium titanyl oxalate powder were obtained by orthogonal experiments at 800 degrees Celsius, 900 degrees Celsius, 1000 degrees Celsius and 3 hours, 4 hours and 5 hours under the condition of research shows that strontium titanate powder fluidity obtained 900 degrees Celsius and 4 hours under the condition of good easy, crystal growth.

4. Conclusion

Experimental results show that the main factors of influence on the purity of strontium titanate including reaction temperature and time, calcination temperature and time. By changing the principle of a single variable, the factors affecting each effect of strontium titanate were tested many times, and finally the optimum technological conditions of preparation of high purity strontium titanate powder by oxalate co precipitation method were finally determined.

(1) the reaction time 4 h, reaction temperature of 60 ℃, Ti: Sr be equal to 1.000:1.005, the highest quality of strontium oxalate, after the calcination of strontium titanate powder particle size uniformity and high purity.

(2) When the calcination temperature is 900 ℃, the titanium oxalate is easy to decompose and crystallize into strontium titanate, the particle size is small, and the purity is high.

5. References

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Acknowledgments

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