Preparation and Characterization of Glass Ceramics Containing SrTiO₃

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Abstract. The glass ceramics containing SrTiO₃ crystals were successfully synthesized by high temperature melting crystallization. The optimum technological formula was determined by orthogonal experiment. The heat treatment system of the glass samples were determined by differential scanning calorimeter analysis (DSC). The effects of heat treatment temperature and time on crystal formation and grain size were discussed in detail. The ideal heat treatment condition is at 950 °C for 3h. The microstructure and phase structure of glass ceramics were analyzed by scanning electron microscope and X-ray diffraction respectively, which indicate that SrTiO₃ crystal were precipitated uniformly in the glass matrix.

1. Introduction

Glass ceramics SrTiO₃ is a more important dielectric material in perovskite structure with compact microstructure. It has eth following functions; higher dielectric number, low dielectric loss, higher insulation resistance, high dielectric constant temperature stability, high deflection electric coefficient and high dielectric frequency stability [1-3]. It is widely used to make such as semiconductor material, microcapacitor with miniature size and large capacity, multilayer substrate, various sensors, memory components and sensing components of computers etc. In recent years, it is widely used in capacitor field. Therefore, SrTiO₃ glass ceramics have very important research value and it become one of the hot spots of energy storage materials. It is widely used in the fields of ceramic capacitor, multifunctional semiconductor element, phased array antenna, microwave tuner, ferroelectric memory material, data storage, signal processing and wireless communication.

At present, there are many methods for the synthesis of SrTiO₃ glass ceramics, including melting method, sol-gel method, hydrothermal method and so on. Homogeneous barium strontium titanate (BST) glass-ceramic has been successfully prepared by sol-gel method in 700 °C for size at about 1.0 microns on the perovskite structure by Jiangying Wang, and the sintering temperature is low. The dielectric constant of BST glass increases with the addition of Zn–B–Si–O glass, and the dielectric constant increases with the increase of sintering temperature, and the dielectric loss of BST glass-ceramics generally increases. With the decrease of grain size, the dielectric peak of BST glass ceramic sample becomes lower and wider [4]. Yu-hsiang Tsai synthesized SrTiO₃ thin film by the
hydrothermal–galvanic couple method, and discussed the effect of different Sr\(^{2+}\) concentration on the film thickness. The Sr\(^{2+}\) concentration reaches its maximum at 0.001 m for the size and thickness of the film. The kinetics of film growth was determined by using the modified Avramy-Erofeev equation. Nucleation controls the formation of SrTiO\(_3\) at high Sr\(^{2+}\) concentrations to form nanoparticles. At low Sr\(^{2+}\) concentration, the grain growth was dominant and larger grains were produced. In addition, the dielectric constant and dielectric loss of SrTiO\(_3\) thin films increase with the decrease of Sr\(^{2+}\) concentration. Hydrothermal/solvothermal growth, sol-gel process, and precipitation have several disadvantages such as expensiveness of equipments and reagents, toxicity of the solvents, and complexity of the processes [5].

The high temperature melting crystallization is the earliest preparation of glass ceramics, and is still widely used now. It inherits the preparation technology of the glass, and the uniformity of heat treatment process. The advantage of melt forming is simple process. Usually the molding methods can be used by blow, pressure, pull, pouring, casting; it is very suitable for glass products with irregular shapes and fine appearance. Industrial production can improve the efficiency. The glass ceramics prepared by melting method almost have no porosity, and have higher density than ordinary ceramic products. Although the melting method has obvious advantages, the size and quantity of the crystal phase in the product are closely related to the overall crystallization capacity and the heat treatment system of the base glass. Therefore, the selection of heat treatment system is conduction to obtaining functional glass ceramics with excellent properties [6-9].

SrTiO\(_3\) glass ceramics were synthesized by melting crystallization, and the effect of heat treatment on grain size and crystal formation was discussed in the paper.

2. Experimental
SrTiO\(_3\), BaTiO\(_3\), TiO\(_2\) and SiO\(_2\) were used as glass raw materials and H\(_3\)BO\(_3\) as additives. Samples were prepared by high temperature melting quenching method according to the orthogonal experimental formula. About 20 g analytical raw materials were well mixed in covered corundum crucibles and placed in an air atmosphere. The mixed materials were heated up to 1400°C for 2 h in resistance furnace with the heating rate of 3°C/min. Subsequently, the melt was transferred into a steel mold, followed by annealing at 450°C for 2 h to obtain the co-made glass precursors. After heat treatment the samples were transformed into glass ceramics. Grind the resulting glass to powder of less than 90 μm, the differential thermal analysis (DSC) of matrix glasses were measured on a SDT2960 differential thermal analyzer temperature measurement range of 200°C - 900°C with the heating rate of 10°C/min. During the measurements Al\(_2\)O\(_3\) was used as a reference. To confirm the crystallization phase, X-ray diffraction (XRD) patterns were performed on a Rigaku2500PCX(Japan) X-ray diffraction apparatus with Cu Ka radiation over the angular range 10-90° in a step size of 4°/min. The microstructure of glass ceramics were characterized by scanning electron microscopy (SEM, JEOL, JSM-7610F) operated at 10kV [10-12].

| The level | BaTiO\(_3\)(mol) | SrTiO\(_3\)(mol) | TiO\(_2\)(mol) | SiO\(_2\)(mol) |
|----------|----------------|----------------|----------------|----------------|
| 1        | 0.70           | 0.30           | 0.07           | 0.20           |
| 2        | 0.60           | 0.40           | 0.75           | 0.15           |
| 3        | 0.50           | 0.50           | 0.80           | 0.10           |

3. Result and discussion

3.1. Optimized design of matrix glass formula
The degree of crystallization is mainly SrTiO\(_3\) with good strength and smooth surface as 1, SrTiO\(_3\) as main crystal phase with strength of 0.8, SrTiO\(_3\) as secondary crystal phase with 0.5 and without SrTiO\(_3\) as 0.3 and so on.
Table 2. Test program and test result analysis.

| Test number | BaTiO₃(A) | SrTiO₃(B) | TiO₂(C) | SiO₂(D) | 900°C / 2h crystallization degree |
|-------------|----------|-----------|---------|---------|----------------------------------|
| 1           | 1        | 1         | 1       | 1       | 0.5                              |
| 2           | 1        | 2         | 2       | 2       | 0.7                              |
| 3           | 1        | 3         | 3       | 3       | 0.3                              |
| 4           | 2        | 1         | 2       | 3       | 0.5                              |
| 5           | 2        | 2         | 3       | 1       | 0.9                              |
| 6           | 2        | 3         | 1       | 2       | 0.6                              |
| 7           | 3        | 1         | 3       | 2       | 0.5                              |
| 8           | 3        | 2         | 1       | 3       | 0.8                              |
| 9           | 3        | 3         | 2       | 1       | 0.6                              |

| K₁          | 1.5      | 2.0       | 2.0     | 2.0     |
| K₂          | 2.0      | 2.4       | 1.8     | 1.8     |
| K₃          | 1.9      | 1.5       | 1.7     | 1.6     |
| k₁          | 0.5      | 0.67      | 0.67    | 0.67    |
| k₂          | 0.67     | 0.80      | 0.60    | 0.60    |
| k₃          | 0.63     | 0.50      | 0.56    | 0.53    |

| Poor R      | 0.5      | 0.9       | 0.3     | 0.4     |

Primary and secondary factors: B > A > D > C

The optimal solution: A₂B₂C₁D₁

Table 3. Optimal formulation of matrix glass.

| BaTiO₃(mol) | SrTiO₃(mol) | TiO₂(mol) | SiO₂(mol) | H₃BO₃(mol) |
|------------|------------|-----------|-----------|-----------|
| 0.60       | 0.40       | 0.70      | 0.20      | 0.20      |

Figure 1. DSC curve of precursor glass sample.
As can be seen from the table 1-2, A factor column: K2 > K3 > K1, B factor column: K2 > K1 > K3, C factor column: K1 > K2 > K3, D factor column: K1 > K2 > K3, so the optimal scheme is A2B2C1D1. As there is no data in the experiment, we supplemented the experiment A2B2C1D1 and found that the degree of crystallization reached 0.95, which was the best. The optimal formulation of matrix glass is shown in Table 3.

3.2. Determine crystallization temperature by differential thermal analysis
The matrix glass samples were prepared according to the optimal formula. The precursor glass samples were subjected to differential scanning calorimetry (DSC) as shown in Figure 1. The figure shows that the crystallization peak at 780°C. According to the DSC curve, determine the heat treatment temperature of, 800°C, 850°C, 900°C, and 950°C.

3.3. Effect of heat treatment temperature and time on crystal phase of glass ceramics
The XRD patterns of glass ceramics at different treatment temperatures are showed in Figure 2(a). As can be seen from the Figure 2(a), the XRD pattern of sample heat-treated at 800°C shows no diffraction peaks characteristic. Continue to heat up to 850°C, strontium titanate has generated, but not the main crystal phase, mainly BaAl2Si2O8 phase. 900°C is given priority to with SrTiO3 phase, BaAl2Si2O8 phase weakened. When the heat treatment temperature is 950°C, the BaAl2Si2O8 phase disappears and only SrTiO3 crystalline phase precipitates out. So 950°C is chosen as the appropriate temperature.

The XRD patterns of glass ceramics at 950°C for different treatment time are showed in Figure 2(b). As can be seen from the Figure 2(b), when the heat treatment time is 2.0 h at 950°C, appear SrTiO3 crystal phase BaAl2Si2O8 coexisting phenomenon at the same time. At 2.5h, the crystal phase of SrTiO3 was enhanced, but the signal of BaAl2Si2O8 was weakened. At 3.0h, SrTiO3 signal was further enhanced and became the main crystal phase, while BaAl2Si2O8 signal disappeared. 3.5h is also the main crystal phase of SrTiO3 (35-0734), and the signal is the strongest in the figure. Therefore, the heat treatment time can be selected as 3.0h to meet our requirements [13-15].

![Figure 2](image)

**Figure 2.** (a) XRD patterns of glass ceramics at different heat treatment temperatures, (b) XRD of glass ceramics with different heat treatment time.

3.4. Effect of heat treatment temperature and time on particle size of glass ceramics
The SEM images of glass ceramics heat-treated at 850°C, 900°C, 950°C and 1000°C are shown in Figure 3. when can be seen from the diagram, less ceramic grain at 850°C and increased grain number at 900°C, the ceramic particle size distribution and modest at 950°C, when ceramic grain coarsening, and some phenomenon of reunion more than 950°C. So 950°C was the heat treatment temperature [16,17].
As can be seen from the Figure 4 that when the heat treatment time is 2.0 h, the crystal particles are very small and unevenly distributed. With the increase of the heat treatment time, the crystal particles grow gradually until the heat treatment time is 3.0 h, and the crystal growth is complete and evenly distributed. However, if the heat treatment time continues to increase, the agglomeration phenomenon will occur. Therefore, the heat treatment time can be selected as 3.0 h [18-20].

4. Conclusions
In this paper, the titanate glass ceramics containing SrTiO₃ crystals were prepared by melting crystallization method, and the process was optimized by orthogonal experiment. The optimal formula was shown in table 3. And discussed the influence of heat treatment conditions on the crystal phase and particle size, the optimum heat treatment conditions are determined for 950°C for 3h. It can be seen from the SEM image of the sample that SrTiO₃ glass ceramics synthesized under this condition, after the crystal phase is precipitated, are evenly distributed in the glass matrix.

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