Morphology of Bi₂WO₆ powders obtained in the presence of fused salts

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Bismuth tungstate (Bi₂WO₆) powders are formed from constituent oxides in the presence of molten chloride and sulphate salts, i.e. 0.5 NaCl–0.5 KCl and 0.365 Na₂SO₄–0.635 Li₂SO₄, in the temperature range from 650 to 900° C. The morphology of powders so obtained depends on the salt system and the experimental conditions. Plate-like particles are obtained by use of the chloride salts. The particle size of the materials is about 5 and 100 μm when prepared below and above the liquidus temperature in the pseudo-binary Bi₂WO₆–chloride salt system respectively. The morphology of the particles obtained by using sulphate salts is complicated. Particles having characteristics of orthorhombic symmetry are obtained in the initial period of the reaction, but they become spheroidal with further heating, finally approaching an oblate form. Mechanisms of morphology changes are discussed and it is concluded that the chief difference in the salt effect is the strong stabilizing effect of (0 1 0) in the chloride salts.

1. Introduction

Particulate materials with shape anisotropy have been used to fabricate grain oriented ferroelectric ceramics by normal sintering [1, 2]. In this method the particles have been aligned by tape-casting and sintered; the morphology of the powder particles has a decisive factor on the orientation of the product. The powders have been synthesized by fused salt synthesis, in which low melting water-soluble salt mixtures are used as a reaction aid [3–6]. Powder particles with shape anisotropy can be easily produced by this method [7] but little information has been published on the relationship between the reaction parameters and the morphology of particles obtained.

This paper deals with the effect of reaction conditions on the morphology of Bi₂WO₆ powder particles. Bi₂WO₆ is a compound with a bismuth layer structure [8] and has an orthorhombic unit cell with $a = 0.5457$, $b = 1.6427$ and $c = 0.5436$ nm [9]. Two kinds of eutectic mixtures, 0.5 NaCl–0.5 KCl and 0.365 Na₂SO₄–0.635 Li₂SO₄, were used as fused salts. Two preparation methods were examined. First, α-Bi₂O₃ and WO₃ were reacted in the presence of the fused salts. This

procedure involved two processes; formation of Bi₂WO₆ by reaction between the raw materials, and growth of Bi₂WO₆ particles after the reaction. Secondly, Bi₂WO₆ powders were mixed with the salts and heated to examine the particle growth process.

2. Experimental procedure

Reagent grade α-Bi₂O₃, WO₃, NaCl, KCl, Na₂SO₄ and Li₂SO₄ · H₂O were mixed with a mechanically driven agate mortar and pestle for 1 h. Fig. 1 shows scanning electron microscope (SEM) photographs of the starting oxides. The Bi₂O₃ particles were needle-like and their size was several scores of a micrometre. The WO₃ powder had aggregate particles of about 10 μm and primary particles of about 0.1 μm. The amount of flux, W, was defined as

$$W = \frac{\text{total weight of anhydrous salts}}{\text{total weight of oxides}}. \quad (1)$$

The mixtures were put into Pt crucibles, heated in a furnace at the desired temperature (between 650 and 900° C) for the desired time period and cooled in air. The mixtures heated above
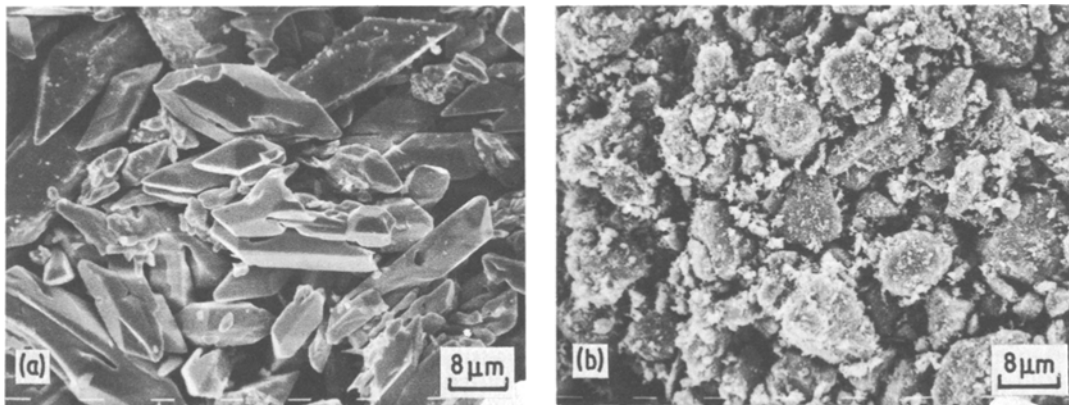
Figure 1 SEM photographs of the starting oxides, (a) Bi_2O_3 and (b) WO_3.

$850°C$ were preheated at $700°C$ for 1 h to complete Bi_2WO_6 formation, because Bi_2O_3 has the lowest melting temperature ($825°C$) in the $Bi_2O_3-WO_3$ system [10]. The salts were washed out with deionized water and the powders were dried, then the phases were examined by X-ray diffraction analysis using Fe$K\alpha$ radiation and the morphology was observed by SEM.

The solubilities of Bi_2WO_6 in the fused salts were determined as follows [11]. Bi_2WO_6 powder, obtained by solid-state reaction between Bi_2O_3 and WO_3 at $800°C$ for 2 h, was sintered at $900°C$ for 24 h. The sintered pellets were embedded in the salt mixtures and heated between 700 and $900°C$ for 3 to 24 h. The amount of Bi_2WO_6 dissolved in the known weight of the fused salts was determined by the difference in weight before and after the heating. The eutectic temperature in the pseudobinary system was determined by differential thermal analysis (DTA).

3. Results

3.1. Morphology of powders formed in the chloride salts.

The formation of Bi_2WO_6 in the chloride salts with $W = 1.0$ was completed within 10 and 5 min at 650 and $700°C$ respectively. Fig. 2 shows the effects of temperature on the morphology of particles. The plate-like particles were obtained between 650 and $900°C$. Below $800°C$ the diameter of the plates was several micrometres and became larger at higher temperatures. Above $850°C$ the diameter of the plates was about $100\mu m$.

Similar temperature effects were observed in the specimens with W between 0.25 and 2.0. That is, small particles of several micrometres width and large ones about $100\mu m$ wide were obtained below and above a certain temperature, which was lowered by the increase in the amount of the fused salts.

Fig. 3 shows the effects of heating time on the morphology of the powder particles at $700°C$. In the initial stage (5 min) plate-like particles were formed and further heating increased the size of the plates.

3.2. Morphology of powders formed in the sulphate salts.

The formation of Bi_2WO_6 in the sulphate salts with $W = 1.0$ was completed within 1 h and 30 min at 650 and $700°C$ respectively, indicating that the reaction rates in the chloride salts were greater than those in the sulphate salts. Fig. 4 shows SEM photographs of Bi_2WO_6 powders heated between 650 and $900°C$ for 1 h. The powder obtained at $650°C$ was a mixture of small and large particles (about 1 and $4\mu m$ respectively), each of which has a morphology characterized by flat faces and well-defined edges and corners. The powder particles obtained between 700 and $800°C$ were spheroidal. Heating at higher temperatures promoted spheroidization and narrowed the particle size distribution. The particles obtained at $850°C$ grew larger and edges between curved facets were formed. Finally at $900°C$ the particles continued growing and their shape changed to oblate.

Fig. 5 shows the effects of heating at $700°C$ on the morphology of particles. In the initial period (10 min), Bi_2WO_6 powders contained large and small particles, both having a crystal shape as shown in Fig. 4a and b. After 30 min heating when the formation reaction was com-
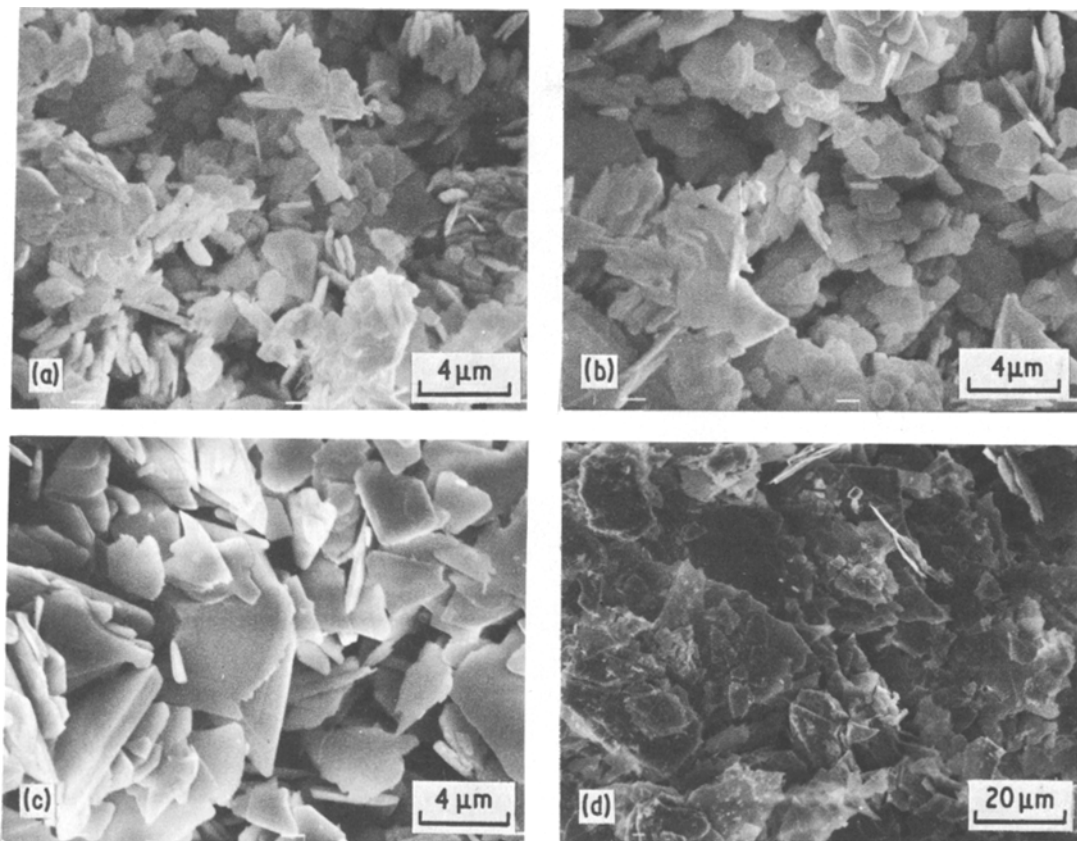
Figure 2 SEM photographs of the Bi_2WO_6 powders obtained by 1 h heating at (a) 650, (b) 700, (c) 800 and (d) 850° C in the presence of chloride salts ($W = 1.0$).

pleted, the particles started to become spheroidal and grew larger, resulting in the narrow particle size distribution.

Fig. 6 shows an SEM photograph of powder obtained at 900° C for 1 h with $W = 9$. The content separated into two portions in the crucible. The bottom part was yellow and the upper one was white. For this particular run with $W = 9$ the amount of fused salts was large and sedimentation of solid particles occurred. The rounded particles shown in Fig. 6 were from the bottom portion and the plate-like particles from the upper one.

3.3. Morphology change in the fused salts.
The lumpy particles obtained by solid state reaction between Bi_2O_6 and WO_3 at 800° C for 2 h (Fig. 7), were mixed with chloride salts ($W = 1.0$) and heated. Fig. 8 shows SEM photographs obtained after heating at different temperatures for 1 h. At 700° C the shape of starting particles was retained but some plate-like particles were observed. High magnification photographs

showed the trace of dissolution along a certain crystallographic direction. The proportion of plate-like particles increased at a higher temperature (800° C, 1 h) or with prolonged heating (750° C, 46 h).

The plate-like particles, which were obtained at 700° C for 1 h in the presence of the chloride salts shown in Fig. 2b, were mixed with the sulphate salts ($W = 1$) and heated at 750 and 800° C. Fig. 9 shows SEM photographs of the powders thus obtained. The plate-like shape was retained but the diameter and thickness were increased by extended heating at higher temperatures. Comparison with Figs 4 and 5 indicates that particle shape is determined by the initial shape when particles grow in the sulphate melt.

3.4. Solubility of Bi_2WO_6 in the fused salts
Fig. 10 shows the phase diagrams of pseudo-binary systems. The solubility of Bi_2O_6 in the fused chlorides is much greater than that in the fused sulphates. Fig. 10 also shows the particle size
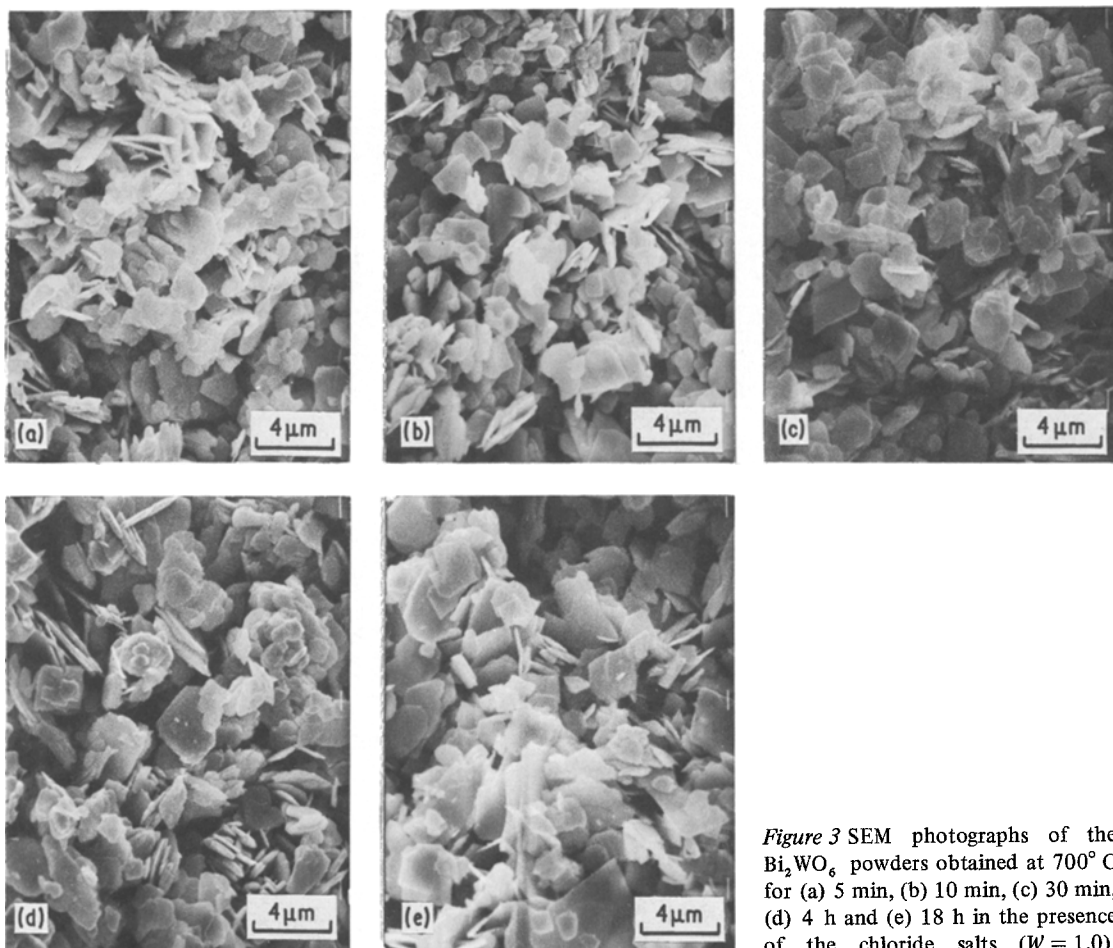
Figure 3 SEM photographs of the Bi_2WO_6 powders obtained at 700° C for (a) 5 min, (b) 10 min, (c) 30 min, (d) 4 h and (e) 18 h in the presence of the chloride salts ($W = 1.0$).

obtained in the chloride salts. The temperature at which the particle size changed abruptly agrees with the liquidus temperature.

4. Discussion

Bismuth tungstate powders obtained by the solid state reaction were mixed with a single salt and were heated at about 30° C above the single salt melting point for 1 h. The particles obtained in NaCl (at 825° C) and KCl (at 800° C) were plate-like, similar to those shown in Fig. 2c. The particles in Li_2SO_4 (at 865° C) and Na_2SO_4 (at 910° C), on the other hand, were oblate, similar to those shown in Fig. 4f. Obviously, the anion species determines the particle shape.

4.1. Formation mechanism of Bi_2WO_6 in the chloride salts

Bismuth tungstate has a layered structure with $(Bi_2O_2)^{2+}$ layers interleaved by $(WO_4)^{2-}$ layers stacked in a $\langle 0 1 0 \rangle$ orientation [9]. X-ray dif-

fraction analysis of a tape-cast sheet made of plate-like particles indicated that $\langle 0 1 0 \rangle$ is perpendicular to the major face of the plate [1]. The chloride salts would have stabilized (0 1 0) so that the plate-like particles resulted. Probably the reaction mechanisms are different below and above the liquidus temperature.

Below the liquidus temperature the unreacted raw materials dissolve in the fused salts and Bi_2WO_6 particles precipitate. Further heating would give more Bi_2WO_6 and increase the particle size. After the formation reaction is completed, the particles continue to grow (Figs 2 and 3). The growth rate, however, is smaller than that in the sulphate salts (compare Fig. 2 and Fig. 9), contrary to usual growth in which crystals with higher solubility grow faster [12]. This unusual behaviour could be explained by the strong (0 1 0) stabilizing effect of the chloride salts. Growth perpendicular to the plate plane at the expense of smaller particles increases the total interfacial energy, because
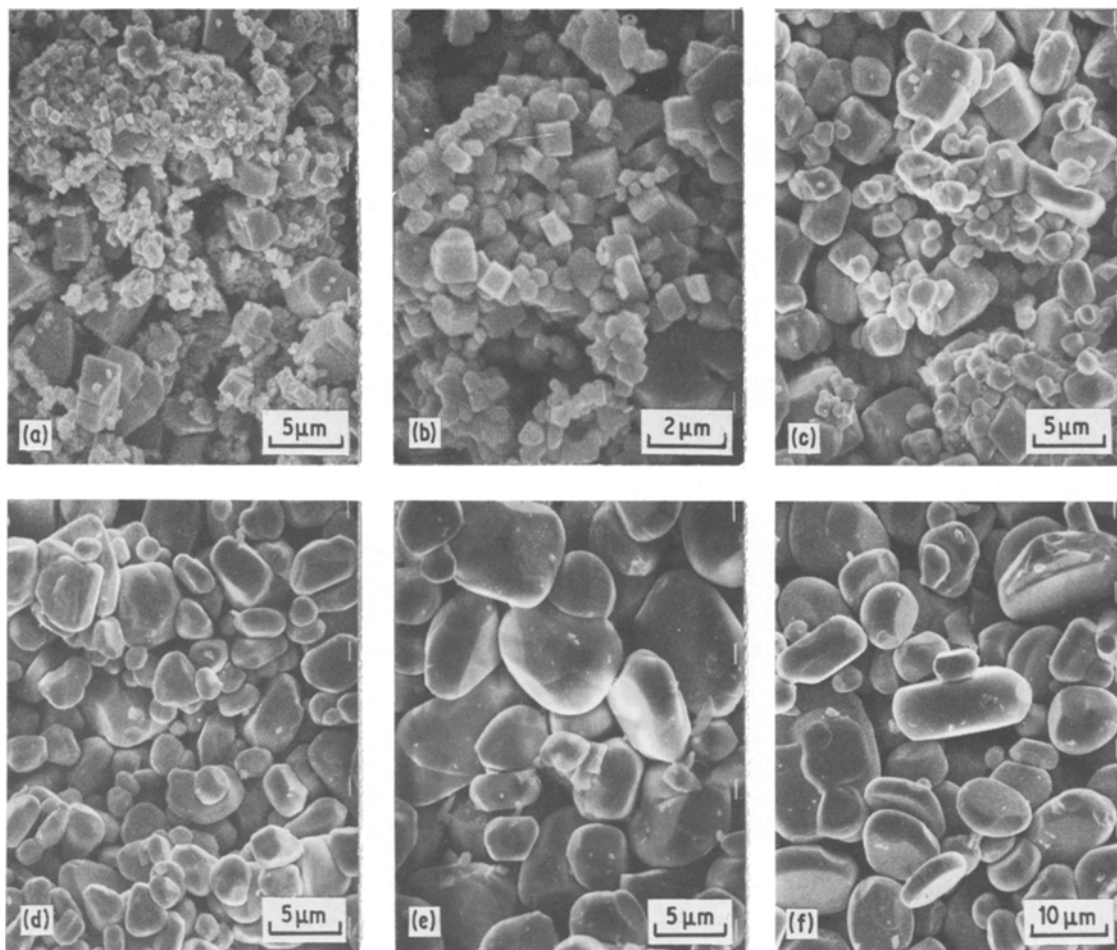
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Figure 4 SEM photographs of the Bi_2WO_6 powders obtained by 1 h heating at (a) and (b) 650, (c) 700, (d) 800, (e) 850 and (f) 900° C in the presence of sulphate salts ($W = 1.0$).

each particle mainly consists of (0 1 0). Growth parallel to the plate plane only decreases the number of faces other than (0 1 0) but the decrease in the number of faces other than (0 1 0) would not contribute to the change in total interfacial energy, thus resulting in the small driving force and low particle growth rate. During cooling to room temperature, Bi_2WO_6 dissolved in the fused salts would precipitate but no nucleation is necessary because solid particles co-exist. These processes (formation and particle growth during heating and precipitation during cooling) would result in the small particle size.

Above the liquidus temperature all oxides are dissolved in the fused salts and Bi_2WO_6 precipitates during cooling. In this process nucleation is necessary and accompanied by supersaturation. The growth rate of the crystals increases with increasing supersaturation. Once the nuclei are formed, the particles grow rapidly until supersaturation vanishes, resulting in the large plate-like particles with well-developed (0 1 0) faces.

When the lumpy Bi_2WO_6 particles were heated with chloride salts, dissolution of Bi_2WO_6 occurs first. The highly anisotropic nature of the interfacial energy would result in a preferential dissolution parallel to ⟨0 1 0⟩ and the trace of dissolution was observed as shown in Fig. 8b. In ordinary Ostwald ripening the decrease in the total interfacial energy is achieved by decreasing the total interfacial area [12]. In this case, however, the decrease of the total interfacial energy is achieved by forming particles with faces of the lowest interfacial energy. Thus, dissolved Bi_2WO_6 was precipitated as plate-like particles, until the lumpy particles disappeared.
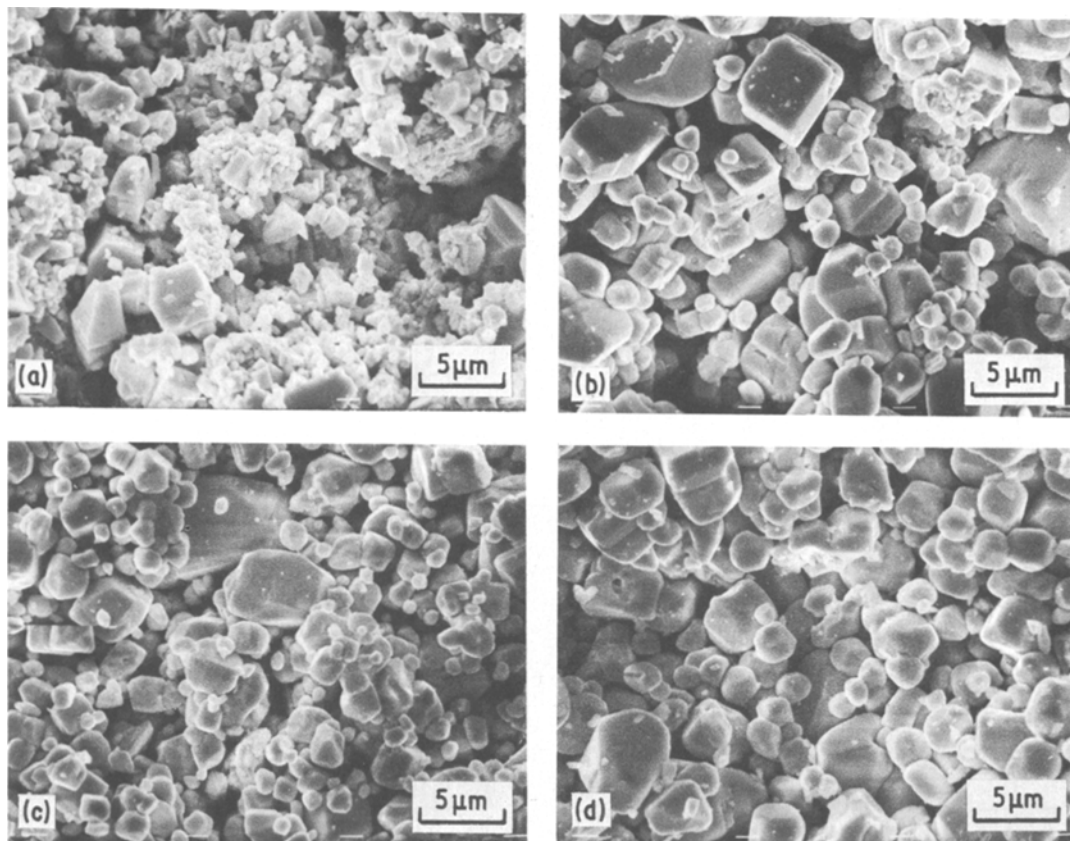
Figure 5 SEM photographs of the Bi_2WO_6 powders obtained by heating at 700° C for (a) 10 min, (b) 30 min, (c) 4 h and (d) 18 h in the presence of sulphate salts ($W = 1.0$).

4.2. Formation mechanism of Bi_2WO_6 in the sulphate salts.

The sulphate salts would stabilize (0 1 0) but the difference in interfacial energy between (0 1 0) and other faces is smaller than in the chloride

salts. The faceted particles (Figs 4a, b and 5a) are formed by the reaction between dissolved raw materials. In this case the kinetics of growth in each face will control the particle shape, as usually observed in single crystal growth [13]. When the formation reaction is completed, spheroidization
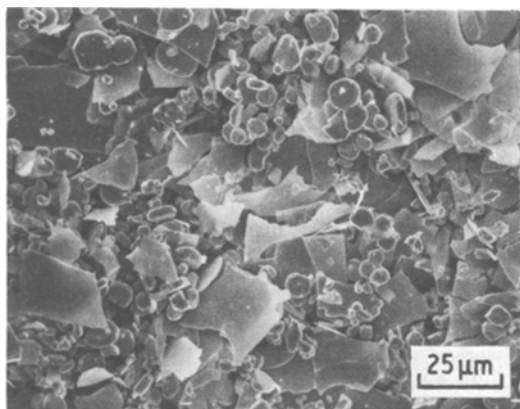

Figure 6 SEM photograph of the Bi_2WO_6 powder obtained at 900° C for 1 h in the presence of sulphate salts ($W = 9.0$).
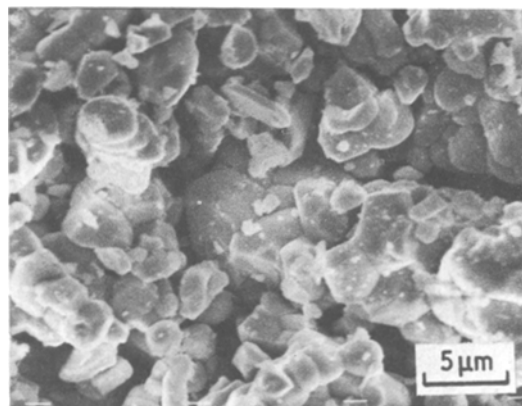

Figure 7 SEM photographs of the Bi_2WO_6 powder obtained by solid state reaction at 800° C for 2 h.
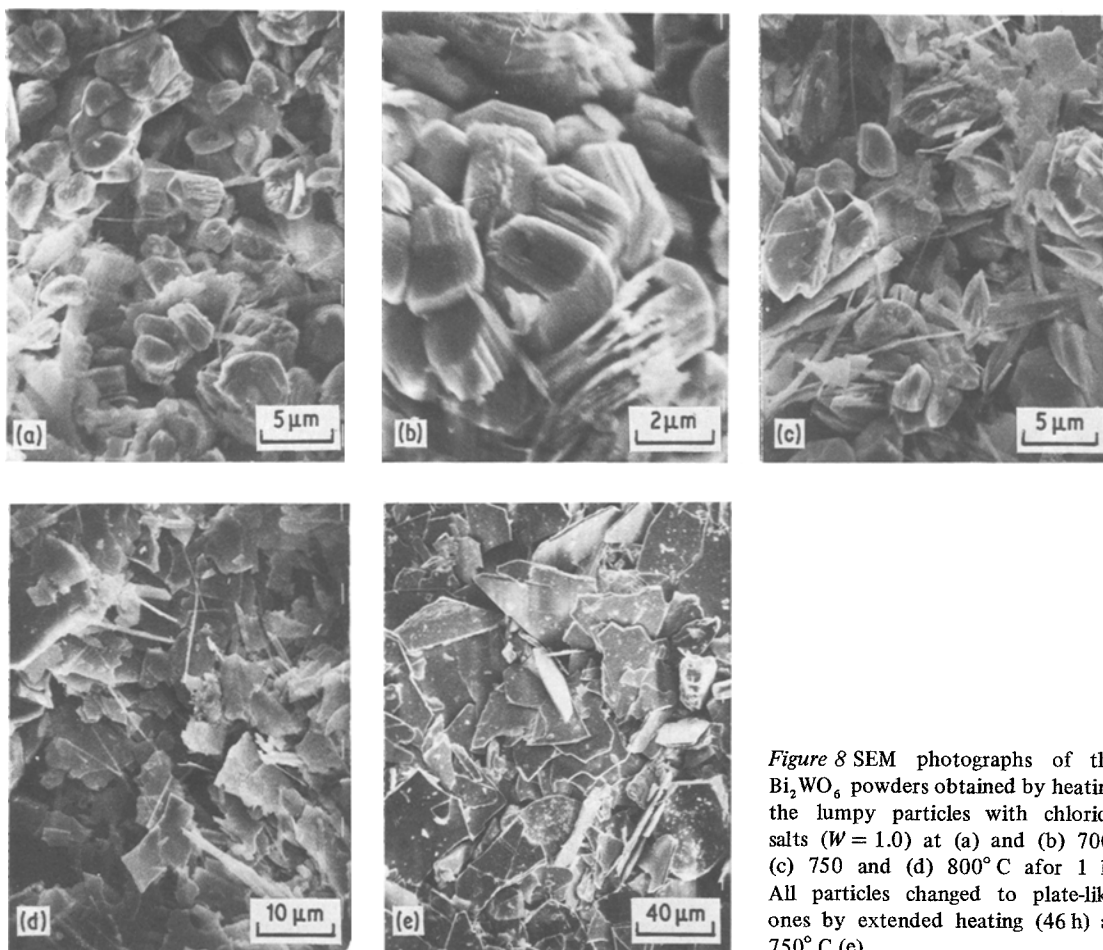
Figure 8 SEM photographs of the Bi_2WO_6 powders obtained by heating the lumpy particles with chloride salts ($W = 1.0$) at (a) and (b) 700, (c) 750 and (d) 800° C afor 1 h. All particles changed to plate-like ones by extended heating (46 h) at 750° C (e).
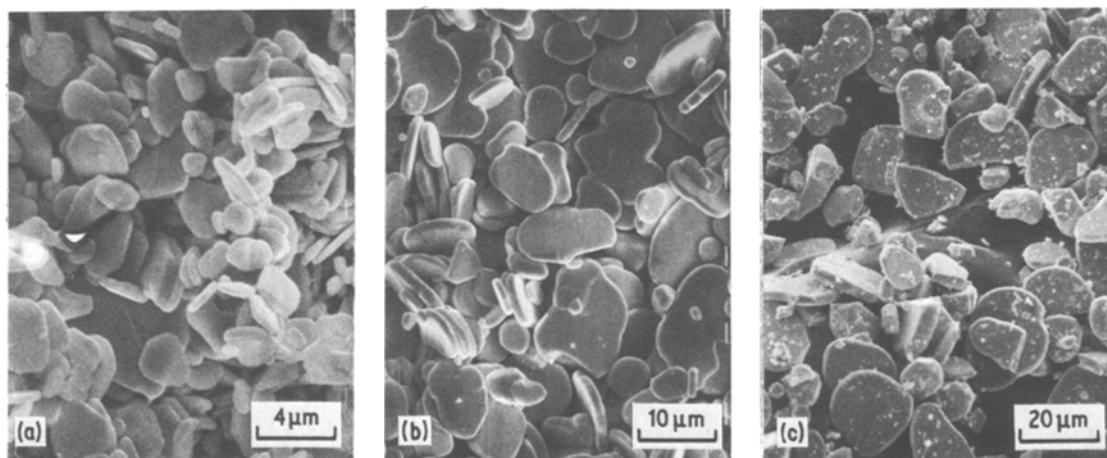

Figure 9 SEM photographs of the Bi_2WO_6 powders obtained by heating the plate-like particles with sulphate salts ($W = 1.0$) (a) at 700° C for 1 h, (b) at 800° C for 1 h and (c) at 800° C for 4 h.
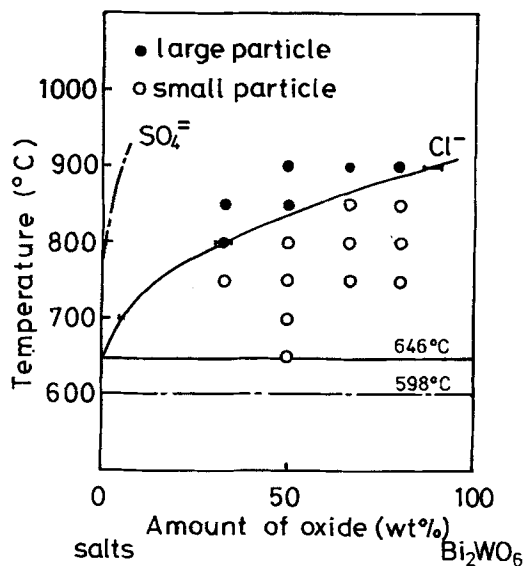
Figure 10 Phase diagram of pseudo-binary systems. The size of the plate-like particles obtained in the presence of the chloride salts is also shown.

occurs by dissolution of Bi_2WO_6 at the edges and corners which can be in equilibrium only with a supersaturated solution. Further heating would cause material transport from small to large particles (Ostwald ripening [12]), resulting in a sharp particle size distribution. As (0 1 0) is considered to have the smallest interfacial energy, the oblate shape (Fig. 4f) is possibly the equilibrium form. The fact that the plate-like particle grew (Fig. 9) would support the view that (0 1 0) has the smallest interfacial energy. In this case the growth rate perpendicular to the plate plane was much larger than in the chloride salts, indicating that the difference in interfacial energy between (0 1 0) and other faces is smaller than in the chloride salts.

The plate-like particles shown in Fig. 6 might have been formed by precipitation of Bi_2WO_6, dissolved in the melt, during cooling. In this sample the solid particles were in the bottom portion and Bi_2WO_6 dissolved in the upper portion should nucleate in the melt. The rapid decrease in the degree of supersaturation immediately after the onset of nucleation would result in rapid growth [13] and also in the plate-like particles, just as in the case of chloride salts above the liquidus temperature, in which the large plate-like particles formed. The fact that plate-like particles were obtained in the sulphate salts used in the solubility measurement, seem to support the above view.

5. Conclusion

The morphology of particles obtained in the presence of the fused salts depends on the reaction conditions. One of the most important factors responsible for the particle shape is the salt effect which produced anisotropy in the interfacial energy. The chloride salts stabilize (0 1 0) more strongly than other faces, resulting in plate-like shape and slow particle growth. Above the liquidus temperatures, the particles are formed by nucleation and growth resulting in the large particles. The sulphate salt has a (0 1 0)-stabilizing effect also, but the difference in interfacial energy between (0 1 0) and other faces is not large. Particles formed during the formation reaction are faceted and the faces are determined by the growth rate of each face. After the formation is completed, the particles start to become spheroidal and approach the equilibrium oblate shape. Particle formation accompanied by nucleation and growth in the sulphate salts results in the plate-like particles.

References

1. T. KIMURA, M. H. HOLMES and R. E. NEWNHAM, *Bull. Amer. Ceram. Soc.* **61** (1978).
2. M. GRANAHAN, M. HOLMES, W. A. SCHULZE and R. E. NEWNHAM, *Commun. Amer. Ceram. Soc.* **64** (1981) C-68.
3. D. G. WICKAM, in "Ferrites: Proceedings of the International Conference" edited by Y. Hoshino, S. Iida and M. Sugimoto (University of Tokyo Press, Tokyo, 1971) p. 105.
4. T. KIMURA, T. TAKAHASHI and T. YAMAGUCHI, *J. Mater. Sci.* **15** (1980) 1491.
5. R. H. ARENDT, J. H. POSOLOWSKI and J. W. SZYMASZEK, *Mater. Res. Bull.* **14** (1979) 703.
6. R. H. ARENDT, *J. Solid State Chem.* **8** (1973) 339.
7. M. HOLMES, R. E. NEWNHAM and L. E. CROSS, *Bull. Amer. Ceram. Soc.* **58** (1979) 872.
8. B. JAFFE, W. R. COOK, Jr and H. JAFFE, "Piezoelectric Ceramics", (Academic Press, New York, 1971) p. 226.
9. R. W. WOLFE, R. E. NEWNHAM and M. I. KAY, *Solid State Commun.* **7** (1969) 1797.
10. S. N. HODA and L. L. Y. CHANG, *J. Amer. Ceram. Soc.* **57** (1974) 323.
11. D. ELWELL and H. J. SCHEEL, "Crystal Growth from High–Temperature Solutions" (Academic Press, London, 1975) p. 114.
12. A. G. WALTON, "The Formation and Properties of Precipitates" (Interscience Publishers, New York, 1967) p. 71.
13. B. LEWIS, in "Crystal Growth", edited by B. R. Pamplin (Pergamon Press, Oxford, 1975) p. 36.