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Preparation of needle-like $TiZrO_4$ and PZT powders

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Needle-like $TiZrO_4$ powder was prepared by reacting TiO_2 and ZrO_2 in the presence of molten chloride (NaCl or KCl) or sulphate (Na_2SO_4 or Li_2SO_4). Either a single-phase $TiZrO_4$ or a three-phase mixture ($TiZrO_4$, ZrO_2 and amorphous TiO_2) was obtained from the chloride or sulphate system. Particle morphology was dependent on heating temperature and duration as well as salt species. Needle-like PZT powder was obtained by reacting needle-like $TiZrO_4$ powder with PbO above 750 °C. The PZT powder obtained at 750 °C was composed of both tetragonal and rhombohedral phases, indicating a wide compositional variation. An increase in heating temperature reduced the degree of compositional variation, but enhanced the deformation of needle-like particles.

1. Introduction

Powder characteristics such as particle size, size distribution, agglomeration state and particle morphology are important for the application of ceramic powders [1, 2]. The control of morphology is difficult, and equiaxed particles are formed by ordinary powder-preparation methods (solid-state synthesis, precipitation, etc.). Powder particles with anisotropic shape (plate- or needle-like) can be prepared by molten salt synthesis for compounds displaying growth anisotropy [3]. Equiaxed particles, however, are obtained for compounds with high symmetry owing to the small growth anisotropy. It is worth investigating methods to control particle shape for such compounds. When a complex oxide is formed by topotactic reaction from simple oxides, particles with anisotropic shape can be prepared by selecting the starting oxide morphology. Acicular $BaTiO_3$ and NiZn- ferrite have been prepared from acicular TiO_2 and Fe_2O_3, respectively [4, 5]. This paper deals with the more complex oxide, $Pb(Ti_{0.5}Zr_{0.5})O_3$ (PZT).

The reaction of acicular TiO_2 with equiaxed PbO and ZrO_2 gave equiaxed PZT particles. We found that rod-shaped $TiZrO_4$ particles were obtained by the reaction between TiO_2 and ZrO_2 in the presence of molten chloride or sulphate. $TiZrO_4$ has orthorhombic α-PbO_2 structure with $a = 0.4804$–0.4809, $b = 0.5412$–0.5483, and $c = 0.5030$–0.5036 nm [6]. The needle axis was found to be parallel to the crystal c-axis. PZT was prepared from the needle-like $TiZrO_4$ powder. This paper deals with the preparation of $TiZrO_4$ and PZT, with special emphasis on the morphology of $TiZrO_4$ and PZT powders.

2. Experimental procedure

Chemically pure reagents were used for oxides (TiO_2, ZrO_2 and PbO) and salts (NaCl, KCl, Na_2SO_4 and Li_2SO_4). TiO_2 and ZrO_2 were mixed in an equimolar ratio in a ball mill for 24 h. The oxide mixture was heated at a temperature between 1100 and 1400 °C for 1 h to examine the phases and morphology of reaction products formed by the solid-state reaction. An equal weight of salt was added to the oxide mixture with an electrically driven agate mortar for 30 min. The mixture was heated in a furnace at a temperature between 1150 and 1250 °C for 1 h. The resultant product was washed with hot distilled water about ten times to remove residual salt.

Needle-like $TiZrO_4$ powder was mixed with $Pb(OH)_2$ by the partial precipitation method [7]. $TiZrO_4$ was suspended in 0.025 M $Pb(NO_3)_2$ solution by ultrasonication, and then aqueous ammonia solution was added to precipitate $Pb(OH)_2$. The mixture was collected by centrifugal sedimentation and heated at 600 °C for 30 min to obtain a $TiZrO_4$ + PbO mixture. No reaction was detected between $TiZrO_4$ and PbO at 600 °C. No excessive amount of PbO over the stoichiometric composition was added. The mixtures were put in a furnace kept at a constant temperature between 750 and 900 °C and soaked up to 60 min.

The phases present were determined by X-ray diffraction (XRD) analysis using CuK_α radiation, and the morphology of the powder particles was observed by scanning electron microscopy (SEM).

3. Results and discussion

3.1. Preparation and characteristics of $TiZrO_4$ powders

The mixture of TiO_2 and ZrO_2 without salt was heated at a temperature between 1100 and 1400 °C for

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1 h. The XRD patterns between $2\theta = 35^{\circ}$ and 37° indicated that the ZrO_2 (2 0 0) and TiO_2 (1 0 1) peaks shifted to higher and lower values of 2θ, respectively, as the reaction temperature increased (Fig. 1). A single phase powder was obtained at 1400 °C. The powder particles obtained were equiaxed.

The development of $TiZrO_4$ particles was almost identical in both NaCl and KCl, although the reaction rate was dependent on the salt species. The reaction between TiO_2 and ZrO_2 was completed by heating for 1 h at 1200 and 1250 °C with NaCl and KCl, respectively. The molten salt not only enhanced material transport, but also changed the reaction process (Fig. 2). The diffraction angles of ZrO_2 (2 0 0) and TiO_2 (1 0 1) remained practically constant during the reaction, and $TiZrO_4$ (0 2 0) peak developed between the two peaks. Comparison of Figs 1 and 2 indicates that solid solutions of ZrO_2 containing TiO_2, and of TiO_2 containing ZrO_2, were formed during the formation of $TiZrO_4$ by solid-state reaction. Although different phase diagrams have been reported in the literature [8–12], TiO_2 and ZrO_2 form limited solid solutions. On the other hand, in the molten salt method, both TiO_2 and ZrO_2 dissolved into the molten salt and $TiZrO_4$ particles precipitated out.

The sample obtained at 1150 °C in KCl (the fraction reacted was about 80%) was composed of almost equiaxed particles (Fig. 3a). Heating at 1200 °C gave needle-like particles (Fig. 3b). This indicates that particles formed during the reaction between TiO_2 and ZrO_2 are equiaxed, and those during the particle growth are needle-like [3]. Although the solubilities of TiO_2, ZrO_2 and $TiZrO_4$ in molten salt are small, and the reaction proceeds in the presence of solid TiO_2, ZrO_2 and $TiZrO_4$ as well as liquid, the solubilities play an important role in determining the phase relations and particle morphology [5]. $TiZrO_4$ particles precipitate when the product of TiO_2 and ZrO_2 concentrations ($[TiO_2]$ and $[ZrO_2]$, respectively) exceeds the solubility product of $TiZrO_4$. The formation of $TiZrO_4$ from TiO_2 and ZrO_2 implies that the product $[TiO_2]_0 \times [ZrO_2]_0$ is larger than the solubility product, where $[TiO_2]_0$ and $[ZrO_2]_0$ are the solubilities of TiO_2 and ZrO_2, respectively.

Particle shape is determined by growth rates normal to various crystal facets. A particle is composed of facets with the slowest growth rate [13]. The growth rate is determined by the atomic configuration at the surface and the degree of supersaturation. The difference in growth rate between facets is largest at lower degrees of supersaturation, but an increase in the degree of supersaturation reduces the difference. In the present case, TiO_2, ZrO_2 and $TiZrO_4$ are present during the reaction (formation stage), and only $TiZrO_4$ is present after the reaction (growth stage). The degree of supersaturation with respect to $TiZrO_4$

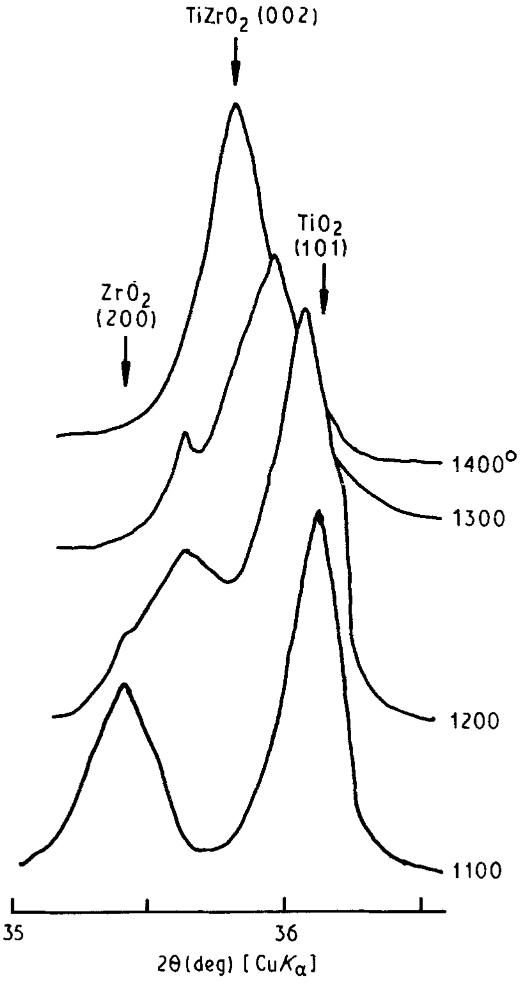

Figure 1 XRD patterns of the reaction products of TiO_2 and ZrO_2 mixtures heated at temperatures indicated for 1 h.

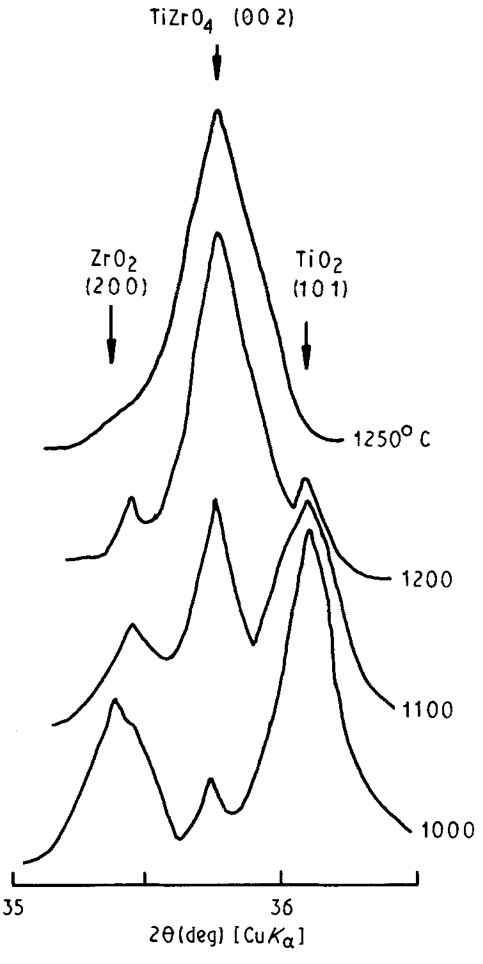

Figure 2 XRD patterns of the reaction products of TiO_2 and ZrO_2 mixtures heated in molten KCl at temperatures indicated for 1 h.

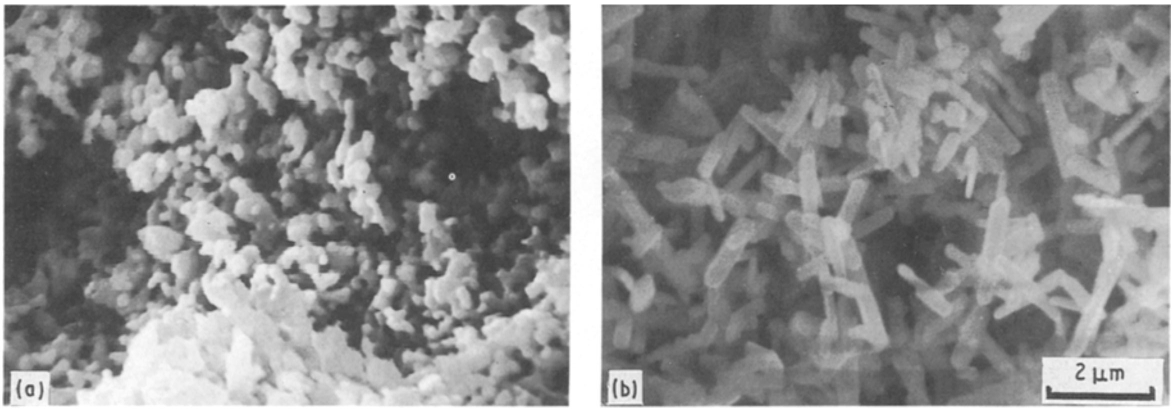

Figure 3 SEM photographs of the powders obtained by heating TiO_2 and ZrO_2 mixture in KCl at (a) 1150; (b) 1200 °C for 1 h.

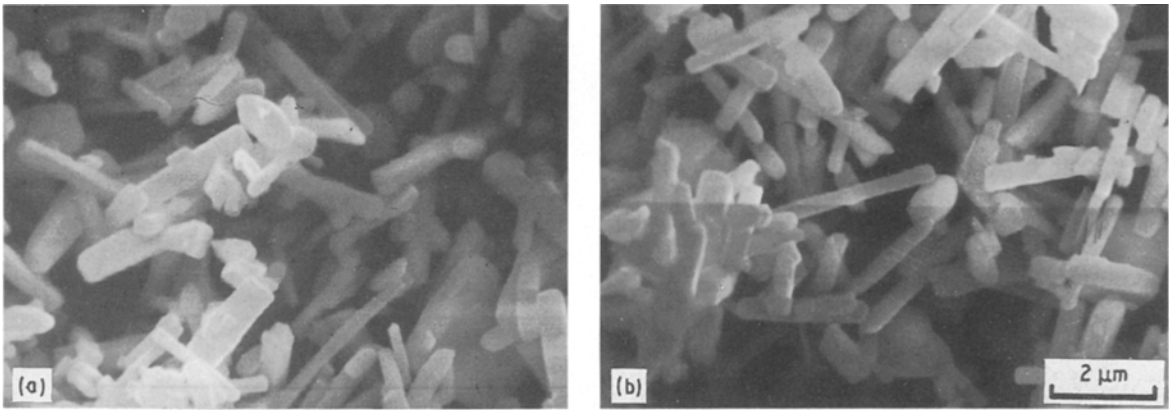

Figure 4 SEM photographs of the powders obtained by heating TiO_2 and ZrO_2 mixture in Na_2SO_4 at (a) 1150; (b) 1200 °C for 1 h.

is determined by the solubilities of TiO_2 and ZrO_2 during the formation stage. As $[TiO_2]_0 \times [ZrO_2]_0 >$ solubility product, the degree of supersaturation is large. The growth rates of various crystal facets are almost the same, resulting in the irregularly shaped equiaxed particles. After the reaction is completed, the degree of supersaturation is determined by the size and the surface free energy of the $TiZrO_4$ particles. A small particle has a larger solubility than a large one. The surface free energy is determined by the atomic configuration at the surface. A $TiZrO_4$ particle with minimum surface energy is composed of the (1 0 0), (0 1 0) and (0 0 1) faces. Small equiaxed particles dissolve and precipitate on large particles. The degree of supersaturation is small during this stage, resulting in needle-like particles.

The intensities of XRD lines for (2 0 0), (0 2 0) and (0 0 2) were almost the same for the sample obtained by the solid-state reaction, but the intensity of the (0 0 2) peak was almost half that of the other lines for needle-like particles. The needle-like particles were preferentially oriented in the sample for XRD analysis. The relative intensity indicates that the needle-axis is parallel to the crystal *c*-axis. The growth rate in the *c*-direction is greater than that in either the *a*- or *b*-directions, resulting in the anisotropic shape.

Needle-like powder particles were also obtained in sulphate salt (Fig. 4). The phases and morphology, however, were slightly different from those obtained in chloride salt. The TiO_2 diffraction peaks disappeared at 1250 °C, but the ZrO_2 peaks still remained. Furthermore, needle-like particles were obtained during the formation stage (Fig. 4a).

The powder obtained at 1250 °C was reheated at 1300 °C for 1 h after removal of the salt. The resultant sample was single-phase $TiZrO_4$. Na_2SO_4 was added to this sample, and the mixture was reheated at 1250 °C for 1 h. The ZrO_2 peaks appeared again. This experiment was repeated by using single phase $TiZrO_4$ obtained by solid-state reaction, and the same result was obtained. The amount of ZrO_2 was larger with Li_2SO_4 than with Na_2SO_4, as judged from the intensities of the ZrO_2 and $TiZrO_4$ diffraction lines.

The presence of ZrO_2 in addition to $TiZrO_4$ might be caused by the difference in solubilities of TiO_2 and ZrO_2 in molten sulphate, i.e.$[TiO_2]_0 > [ZrO_2]_0$. In this case, the excess TiO_2 dissolves until $[TiO_2] \times [ZrO_2]_0 =$ solubility product holds. The amount of TiO_2 dissolved in the sulphate is larger than that of ZrO_2, and excess ZrO_2 is present as solid particles. TiO_2 dissolved in the molten salt remains as amorphous TiO_2 after removal of the salt by washing with water. Thus, heating at 1300 °C after salt removal resulted in the single-phase $TiZrO_4$. The degree of supersaturation with respect to $TiZrO_4$ is small during the formation stage, since $[ZrO_2]_0$ is small, resulting in the formation of needle-like particles during this stage.

3.2. Preparation and characteristics of PZT powders

The size and aspect ratio of needle-like $TiZrO_4$ were dependent on the heating temperature and duration, the amount of salt and the salt species. The particles with the largest aspect ratio were obtained by heating the oxide mixture at 1200 °C for 1 h with an equal weight of NaCl. These were used for the preparation of PZT (Fig. 5).

PbO was completely consumed by heating the mixture above 750 °C for 30 min. PZT particles were needle-like, but were composed of small primary particles (Fig. 6). An increase in heating temperature increased the size of primary particles and reduced the length of the needles. Many nuclei formed at the surface of $TiZrO_4$ particles, resulting in polycrystalline needle-like particles. Heating at high temperatures enhances the material transport, resulting in an increase in primary particle size. Furthermore, heating at high temperatures reduces the aspect ratio, since this morphology is not stable for compounds with high symmetry [14].

PZT powder particles obtained were not single phase, but had wide compositional variation. Fig. 7 shows the XRD profiles of PZT obtained by heating the mixture at various temperatures for 30 min. Tetragonal and rhombohedral phases coexisted in the sample heated at 750 °C. The amount of rhombohedral phase decreased with increasing temperature. The boundary between tetragonal and rhombohedral phases is located at $Pb(Zr_{0.53}Ti_{0.47})O_3$ [15], and so the overall composition of our sample lies in the tetragonal phase field. The XRD profiles shown in Fig. 7 indicate that our PZT powders are of a wide variety of compositions, although increasing the heating temperature reduced this variability. The particles obtained at 900 °C had a smaller aspect ratio than those at 750 °C, but the width of needle was not changed. This fact indicates that the decrease in compositional variation occurs within each particle.

Kakegawa *et al.* [16] reported that the compositional variation was reduced by using a spray-dried $TiZrO_4$ powder. Their work implies that prereacted TiO_2–ZrO_2 mixtures result in a minimized compositional variation. Although they did not report the

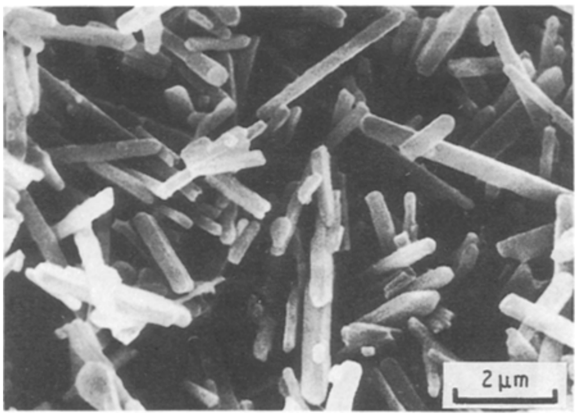

Figure 5 SEM photograph of $TiZrO_4$ powder used for the preparation of PZT.

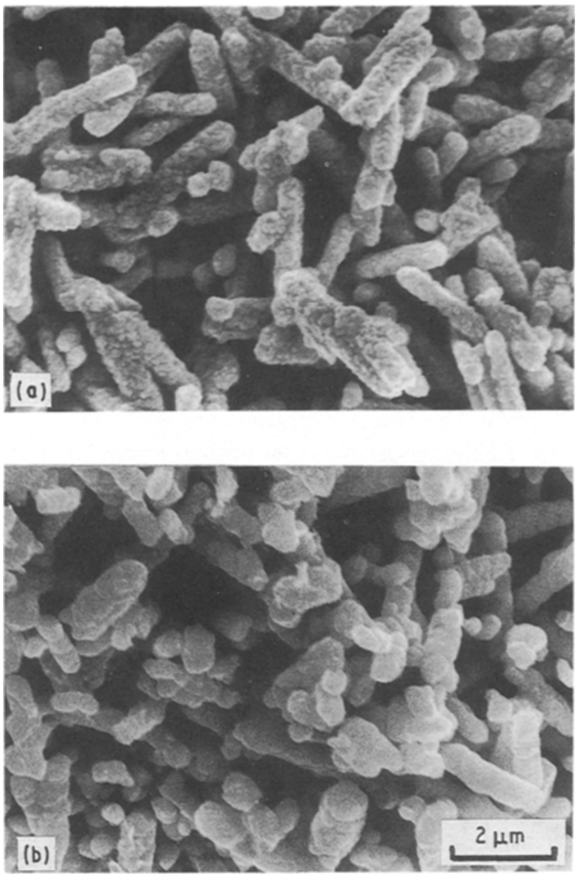

Figure 6 SEM photographs of PZT obtained by heating the needle-like $TiZrO_4$ and PbO mixture at (a) 750; (b) 900 °C for 30 min.

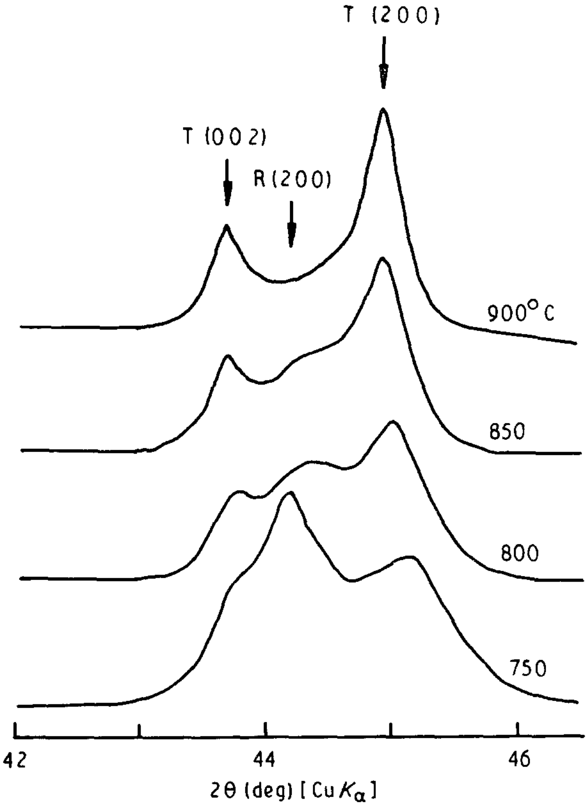

Figure 7 XRD profiles of powders obtained by heating $TiZrO_4$ and PbO at temperatures indicated for 30 min. T and R indicate tetragonal and rhombohedral phases, respectively.

particle size of their $TiZrO_4$ powder, the large size of the $TiZrO_4$ particles used in our experiment might be responsible for the wide compositional variation. Several intermediate compounds are observed during the formation of PZT from mixtures of PbO, TiO_2 and ZrO_2, and $PbTiO_3$ is formed at an early stage of the reaction [17]. Although no intermediate phases were detected in our reaction products, the presence of a wide compositional variation suggests that Ti- or Zr-rich PZT is initially formed in $TiZrO_4$ particles, and Zr- or Ti-rich PZT is formed from the remaining $TiZrO_4$ at a later stage.

4. Conclusions

Needle-like $TiZrO_4$ powder was prepared by molten salt synthesis. The needle axis was parallel to the crystallographic *c*-axis, indicating that the growth rate normal to (0 0 1) was larger than that normal to (1 0 0) or (0 1 0). Chloride salt (NaCl or KCl) gave single-phase $TiZrO_4$ powder, but sulphate salt (Na_2SO_4 or Li_2SO_4) resulted in a three-phase mixture, namely $TiZrO_4$, ZrO_2 and amorphous TiO_2, after salt removal. The difference in solubilities of TiO_2 and ZrO_2 is responsible for the presence of ZrO_2 and TiO_2 in the latter case.

Needle-like PZT, which was obtained by reacting needle-like $TiZrO_4$ with PbO above 750 °C, was composed of both tetragonal and rhombohedral phases. However, increasing the heating temperature decreased the degree of compositional variation, but also enhanced the deformation of needle-like particles.

Acknowledgements

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