

Influence of the Calcination Temperature and Fuel Composition on Synthesis of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ by Solution Combustion Method for High Proton conductivity

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Abstract

Yttrium-Doped Barium Zirconate (BZY20) powders were synthesized by the solution combustion method, using two different fuels (urea and citric acid). The ignition of the reagent mixture with urea takes a longer time and the maximum temperature is higher than using citric acid. The theoretical calculations of exothermic heat and adiabatic flame temperatures indicate favorable conditions for combustion to occur. X-ray diffraction patterns showed formation of only perovskite phase for the samples synthesized with both of fuels. The crystallite sizes are in the range of 24–28 nm, with smaller values when citric acid was used as fuel. Scanning electron microscopy showed the presence of small agglomerates, formed by fine particles of different shapes and the size of BZY20 nanoparticles obtained using citric acid (30–35 nm) was so smaller and more uniform than those obtained using urea (40–50 nm), and their BET surface areas are 30.9 and 20.57 m²/g, respectively. calcination is an essential step for a good crystallization of perovskite pure phase, which result showed 1150°C for 5 h.

Keywords: BZY20, perovskite, solution combustion synthesis, nanocrystalline

1. Introduction

Perovskite proton-conducting oxides have been widely investigated because of their promising applications in a variety of electrochemical devices such as fuel cells, steam electrolysis, hydrogen separation and hydrogen sensors [1]. Figure 1 shows the perovskite structure.

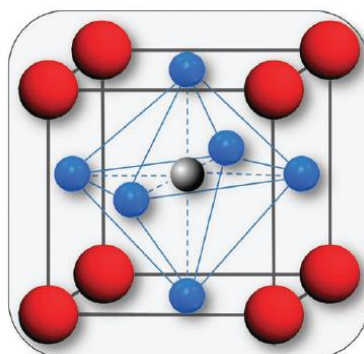


Figure 1. Perovskite Structure

Among them, barium zirconate has been suggested to offer important benefits for such applications because of its chemical stability and high bulk conductivity [2]. The

conventional method of preparing this type of ceramic is to perform a solid state reaction from a stoichiometric mixture of barium carbonate, zirconium and yttrium oxides at temperatures higher than 1000 °C. This method is relatively simple but timeconsuming, energy intensive and leads directly to materials of large grain size in which grain boundary effects are significant. However, nanoparticles are essential for good sinterability and for preparation of fully densified materials [3]. In addition to the solid state route, several wet chemical techniques like coprecipitation [4], oxidant-peroxo [5], spray pyrolysis [6] and the Pechini method [7] or combustion synthesis [8] have been employed to obtain ultra fine and more homogeneous powders. Among the main techniques for generating nanoparticles via the wet chemical route, solution combustion is the one that stands out. This simple technique has many advantages: homogeneous mixing, good stoichiometric control, production of active submicron-size particles in a relatively short processing time, and it involves a combustion process initiated at low temperatures, which makes use of the heat energy liberated by the exothermic reaction between fuel (e.g. urea, glycine, citric acid) and nitrate ions. The parameters that influence the reaction product are the type of fuel, the fuel to oxidizer ratio, and the ignition temperature. Use of suitable fuel in combustion syntheses ensures stability of the chemical composition and high quality of products, and produces non-toxic gases.

Combustion synthesis routes are inspired by the work of Pechini [9]. In the Pechini method, chelating occurs between complex cations and acid like citric acid, which is one of the leading basic chemical reactions as shown in Figure 2.

Alternatively, in modified Pechini synthesis routes, different chelating or combined chelating agents are employed [10]. It seems that what makes difference in the performance of these material is the difference in the strength of bond formation with central atom of complex. So, various complexing agents behave differently, which should be considered. These agents contain carboxylate or amine groups which are essential for the water-soluble complex precursor synthesis route. Citric acid contains carboxylate group, while urea contains aliphatic amine group. So they would behave differently in the methods of synthesis according to their ability in bond formation in complexes [11].

The synthesis typically consists of four steps: (i) formation of organometallic complexes in solution, (ii) solvent evaporation and gel formation, (iii) auto-combustion (pyrolysis) followed by (iv) a heat treatment of the obtained powder [12]. Among several chelating agents, ethylene-diamine-tetra-acetic acid (EDTA) and citric acid (CA) or urea are used most frequently [12]. Due to its higher chelating power, a far more extensive range of cations can be chelated with EDTA compared to CA. Possessing three carboxyl groups and one hydroxyl group, however, CA is the chelating agent with the stronger gelation ability. The sole use of CA as a chelating agent, however, may result in a highly exothermic, non-uniform combustion reaction, adversely affecting the morphology of the powder. For these reasons CA and EDTA are often employed as combined chelating agents [13].

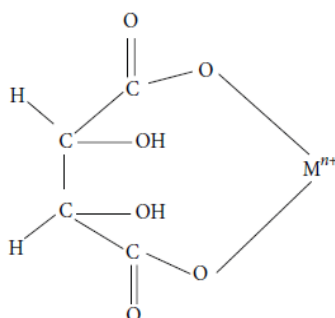


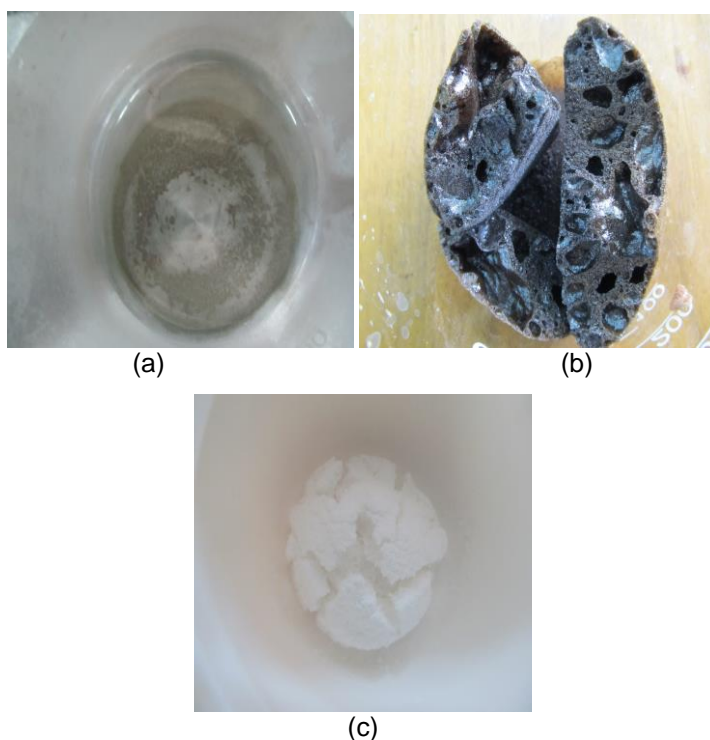
Figure 2. Chelating between Complex Cations and Acid Like Citric Acid

Therefore, the present work is an attempt to study this temperature-dependent transformation of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ powders. It is a try to visualize the correlation of the crystalline structure the BZY20 synthesized by solution combustion method. Moreover, the influence of the calcination temperature and fuel composition on the structural of the perovskite BZY20 powder have been studied and discussed herein.

2. Experimental Procedure

2.1. Powder Preparation

$\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ (BZY20) precursor nanopowder was prepared by a combustion method. Stoichiometric amounts of $\text{Ba}(\text{NO}_3)_2$, $\text{ZrO}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ first were dissolved in deionized water. Subsequently a required amount of ethylenediamine-tetraacetic acid (EDTA) was first dissolved into aqueous NH_4OH and an appropriate amount of citric acid (urea) added to the solution; then citric acid (urea) /ethylenediamine-tetraacetic acid/ NH_4OH solution were added metal nitrates solution and the pH adjusted to 6. The molar ratio of ethylene diamine-tetraacetic acid/citric acid (urea) /metal ions was 1 : 1.5 : 1 and then heated on a hot plate until it turned into a viscous liquid, just below $100\text{ }^\circ\text{C}$. When transparent gels were obtained, they were dried in an oven at $140\text{ }^\circ\text{C}$ for 24 h. The Water evaporated and the residue formed brown foam which then ignited to leave crude precursor as a very fine nanopowder. Then the as-prepared powders were calcined at three temperatures $900\text{ }^\circ\text{C}$, $1150\text{ }^\circ\text{C}$ and $1300\text{ }^\circ\text{C}$ for 5 h in air to form a pure perovskite phase BZY20. Figure 3 shows preparation of BZY20 powder by solution combustion synthesis.



**Figure 3. Preparation Of BZY20 Powder by Solution Combustion Synthesis
(a) Gel (b) Foam (c) Calcined Powder**

2.2. Thermodynamic Calculations

The enthalpy of combustion reaction can be expressed as:

$$\Delta H_{298}^0 = (\sum n\Delta H_{f,298}^0)_{products} - (\sum n\Delta H_{f,298}^0)_{reactants} \quad (1)$$

and

$$\Delta H_{298}^0 = (\sum nC_p)_{products} \cdot dT \quad (2)$$

Where n is the number of moles of each species, ΔH_f^0 is the enthalpy of formation, C_p is the heat capacity and T is the adiabatic flame temperature. Using the thermodynamic data for reactants and products found in the literature data and calculating the C_p of doped perovskites according to the equation [14]:

$$C_{p,perovskites} = \sum x_i C_{p,binaryoxides} \quad (3)$$

Where x_i is the stoichiometric coefficient of the perovskite formation reaction from its binary oxides, it was possible to determine the enthalpy of combustion for each reaction, as well as the adiabatic flame temperatures.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were recorded in a Rigaku Miniflex II diffractometer, with $Cu\alpha$ radiation and monochromator, with speed of 2° min^{-1} . The crystallite sizes (D_{XRD}) and microstrain (ϵ) of the calcined samples were calculated using the model proposed by Williamson and Hall [15], by means of the following formula:

$$\beta \cos \theta / \lambda = 1 / D_{XRD} + 4\epsilon \sin \theta / \lambda \quad (4)$$

Where θ is the diffraction angle, λ is the wavelength of the incident radiation and β is the full width at half maximum (FWHM) of the peak. Plotting the $\beta \cos \theta / \lambda$ versus $4 \sin \theta / \lambda$ straight line yields the crystallite size from interception with the ordinate and microstrain from the slope. The calculus was done using the FullProf software.

Surface area of the powders (BET method) and mesopore size distributions (BJH method) have been determined by nitrogen adsorption/desorption measurements at 77 K, using a Sorptomatic 1900 Carlo Erba Instrument. All samples were pre-treated in vacuum at 250 °C for 1.5 h prior to the measurements. The specific surface areas were calculated by the Brunauer-Emmett-Teller (BET) equation using the data in the P/P_0 range of 0.09–0.3 and outgas temperature of 250 °C. The specific surface area (SSA) was converted into particle size, assuming that the particles are closed spheres with smooth surface and uniform size using

$$D_{BET} = 6000 / d_{th} S_{BET} \quad (5)$$

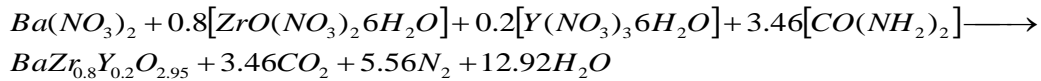
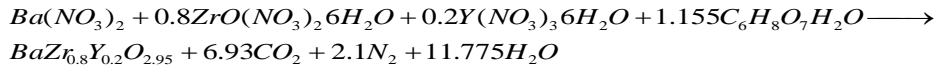
Where d_{th} is the theoretical density of the material under consideration, D_{BET} is the average particle size in nm, and S_{BET} is the specific surface area expressed in $\text{m}^2 \text{ gm}^{-1}$.

The microstructure of the powders was investigated by scanning electron microscopy (SEM) (Leica Cambridge S 360). The acceleration voltage was 15 KV, using backscattering electron.

3. Results and Discussion

3.1. Thermodynamic Calculations

According to the principle of propellant chemistry and considering that N_2 , CO_2 and H_2O are the main gaseous products evolved, the combustion reactions of each process can be expressed as follows:

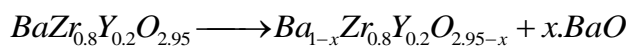


The enthalpies of combustion for each reaction previously described, as well as the adiabatic flame temperatures. All combustion reactions are exothermic and supply the heat needed for the synthesis reaction. The adiabatic flame temperatures are supposed high enough to promote the perovskite synthesis. As expected, the measured combustion temperatures are lower than the theoretically calculated values due to radiative losses, heating of air, and incomplete combustion of the reaction mixture,. the calculated values of heat of combustion and adiabatic flame temperatures for perovskites synthesized with urea are higher than those derived from citric acid route. This may be attributed to an inhomogeneous precursor mixture forming an unstable gel. In such case, the combustion heat can be dissipated to the surrounding colder region where the fuel/oxidant rate is not favorable for combustion and consequently the flame temperature would come down [16].

3.2. Effect of Calcination Temperature

Figure 2 shows X-ray diffraction patterns of BZY20 powder synthesized by the citrate/ethylene-diamine-tetraacetic acid complexing method. It has been reported that the citrate/ethylene-diamine-tetraacetic acid complex finishes its reaction at around 900 °C [17]; therefore, the as-synthesized powders were calcined at 900 °C for 5 h. However, $BaCO_3$ still remains, as shown in Figure 4 and If were calcined at 1150°C for 5 h, produces an almost phase-pure BZY20 powder with an ultra-fine crystallite size (20-40 nm), and with a low level of organic residues. Calcined powder in the temperature of 1300 °C, has secondary phase Y_2O_3 .

At high temperature barium is easily lost from BZY20 leading to the formation of barium deficient phases and BaO [18] according to :



Then, higher Ba losses cause decomposition of this perovskite in BaO , ZrO_2 and Y_2O_3 .

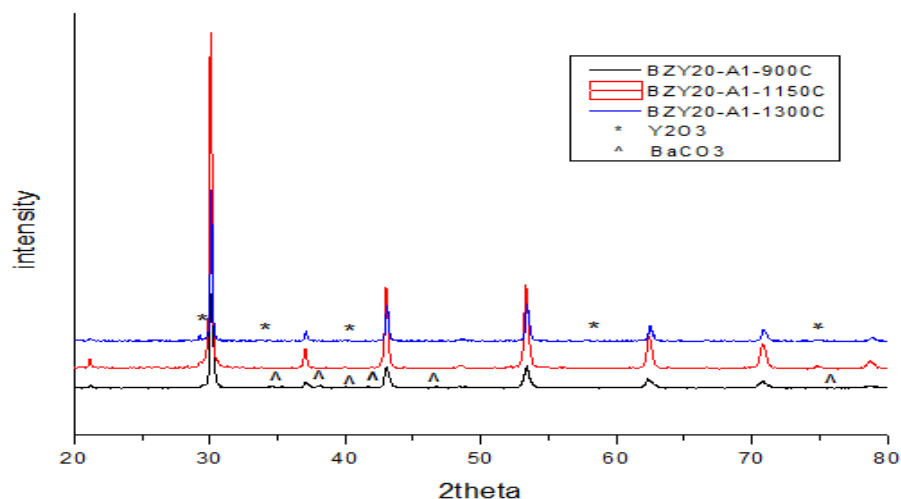


Figure 4. XRD Data of the BZY20 Powders Synthesized by the citrate/ethylene-diamine-tetraacetic Acid Complexing Method and Calcined at (a) 900°C for 5 h, (b) 1150°C for 5h and (c) 1300°C for 5 h, and pH=6

3.3. Effect of Fuel Composition

The XRD patterns of the nanocrystalline powders synthesized by citric acid and urea are shown in the Figure 5. The powders synthesized with urea, and citric acid have diffraction peaks that can be indexed well with the reference of perovskite structure BZY20 which is a cubic crystal system with nanocrystallite. Therefore, the temperatures of combustion between the fuels and metal nitrates were optimum for the formation of the pure phase. The Table 1 shows the average crystallite sizes of the powders as-prepared and calcined, which were calculated from XRD data using the Williamson-Hall equation, and the lattice parameters. It can be seen that the calcinations of the powders at 1150 °C and 5h increase the sizes of the crystallites.

Table 1. Average Crystallite Size of Powders Synthesized by Solution Combustion as Prepared and Calcinated

Complexing agent	as-prepared (nm)	Calcination of 1150 °C / 5h (nm)
Citric acid	7.3	24.7
urea	10.9	28.66

3.4. Particle Size and Specific Surface Area

Table 2 shows the BET surface area of powders and the particle size calculated from (5) using BZY20 density of 6.21 g/cm³. A large particle size calculated from surface area compared to the crystallite size measured by XRD illustrates the rate of agglomeration of the particles. The surface area was higher for the citric acid complexing agent (30.9) compared to urea (20.57) which is in agreement with the size of the nanoparticle, as the particle size becomes smaller, the specific surface area is increased. Using urea as fuel yields powders with low specific surface area and hard agglomerates, because of the formation of stable polymeric intermediates that prevent the dissipation of heat and thereby sintering the oxides during combustion [19].

Table 2. BET Surface Area of Powders and the Particle Size Versus Annealing Temperatures

Complexing agent	S_{BET} (m ² /g)	D_{BET} (nm) T=1150°C
Citric acid	30.9	31.25
urea	20.57	46.9

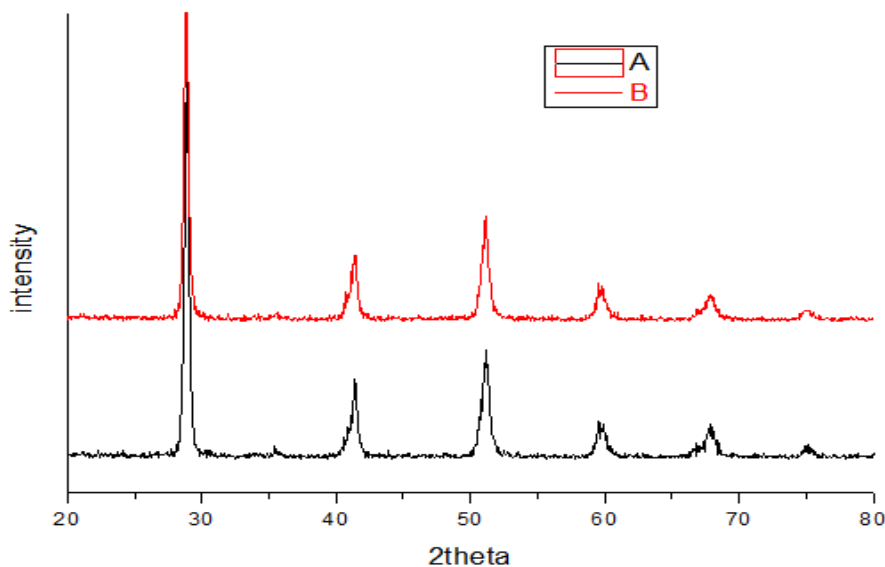


Figure 5. XRD Data of the BZY20 Powders Synthesized by Solution Combustion Method with Fuel (A) Citric Acid, (B) Urea

3.5. SEM Observations

Figure 6 presents the SEM images of BZY20 nanoparticles obtained by solution combustion with the fuels citric acid and urea, which reveal agglomerated, porous, and sponge-like morphologies of the particles, these characteristics are reported in the scientific literature for the solution combustion synthesis, this is due to evolution of the large amount of gaseous products during combustion, which produces highly porous voluminous powders, and these parameters dependent of fuel used in the synthesis. The urea shows nanometric crystals of size bigger than the citric acid, which is consistent with the values calculate from XRD patterns by Williamson-Hall equation. Therefore, these results indicate that a change in the fuel used in the synthesis lead to significant changes in the microstructure of the powders.

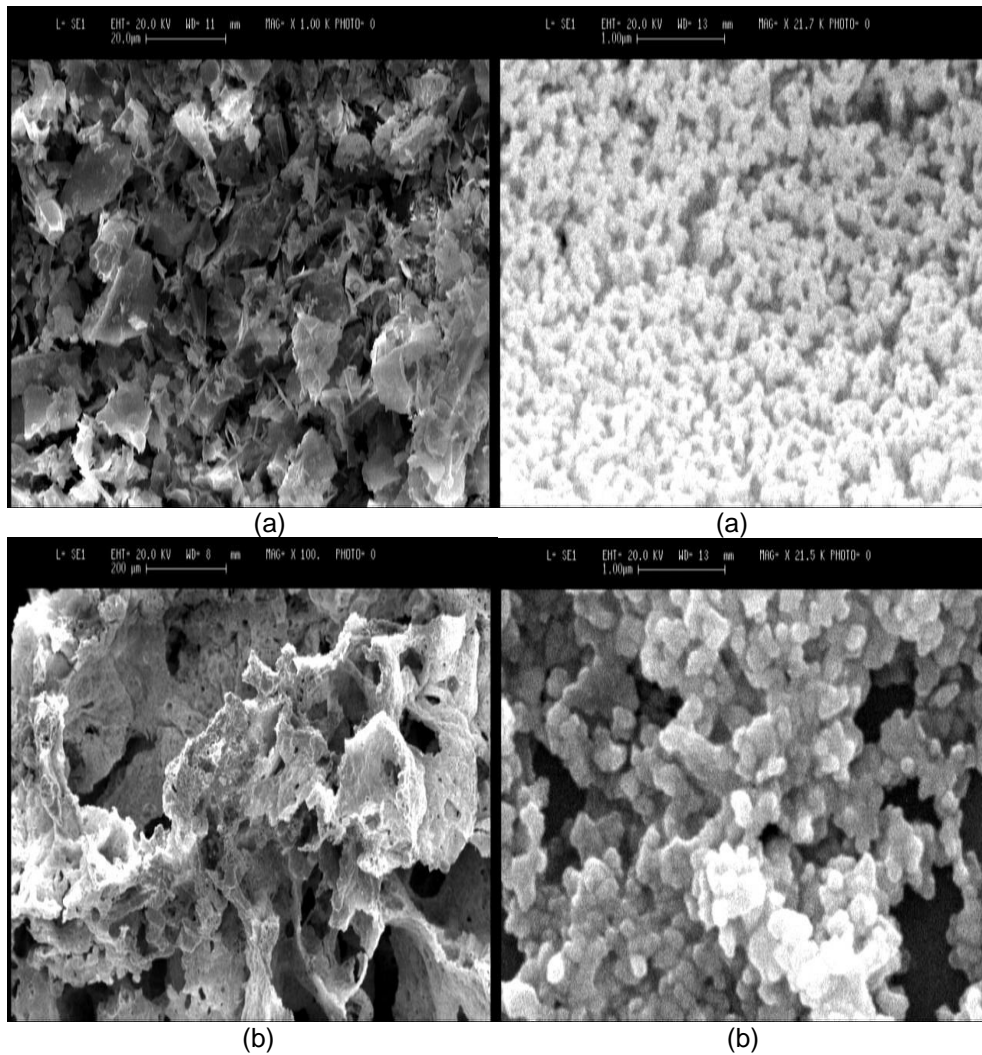


Figure 6. SEM Images of BZY20 Nanoparticles Prepared by (a) Citric Acid and (b) Urea

4. Conclusions

In this work, $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ BZY20 nanopowders has been synthesized by solution combustion using urea, and citric acid, and different calcination temperatures. The following was found.

(a) According to Thermodynamic calculations, using the citric acid lowers the formation temperature of BZY20. So citric acid as a fuel of reaction at lower temperatures and shorter time is introduced.

(b) With increasing calcination temperature up to 1300°C , high intensity and sharp peaks of BZY20 are observed in both samples that shows very high crystallization at this temperature, but the optimum calcination temperature was 1150°C for 5 h which produces a phase-pure BZY20 powders.

(c) According to electron microscope images, the size of BZY20 nanoparticles obtained using citric acid (30– 35 nm) was so smaller and more uniform than those obtained using urea (40-50 nm), and their BET surface areas are 30.9 and $20.57 \text{ m}^2/\text{g}$, respectively.

It was shown that when the combustion reaction produces a great amount of gases and the porosity.

(d) Also, according to XRD patterns, the small average crystallite sizes of 28.66 nm (urea), and 24.7 nm (citric acid) indicates.

(e) This technique is presented as a rapid and economical alternative for preparation of ceramic materials used as high proton conductors.

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