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Structure and properties of nanocrystalline $BaHfO_3$ synthesized by an auto-igniting single step combustion technique

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Abstract

High quality nanoparticles of barium hafnate have been synthesized using an auto-ignition modified combustion technique. The nanoparticles thus obtained have been characterized by powder X-ray diffraction, thermo gravimetric analysis, differential thermal analysis, Fourier transform infrared spectroscopy and transmission electron microscopy. The XRD studies have shown that the as-prepared $BaHfO_3$ powders are phase pure. The particle size of the as-prepared powder was in the range 20–50 nm. The nanopowder could be sintered to 95% of the theoretical density at 1650 °C for 2 h. The ultrafine cuboidal nature of nanopowders with small degree of agglomeration improved the sinterability at relatively lower temperature and time. The microstructure of the sintered surface was examined using scanning electron microscopy. The dielectric constant (ε_r) of 30.8 and loss factor (tan δ) of 2.3×10^{-3} were obtained at 1 MHz.

Keywords: Nanoparticles; Combustion synthesis; Perovskites; Barium hafnate; Sintering

1. Introduction

The syntheses of nanostructured materials have generated great excitement and expectations in the past few years. Because of the extremely small dimensions, a large fraction of atoms in these materials are located at grain boundaries or surfaces interfacial component, leads to outstanding characteristics that bulk coarse-grained materials do not possess [1]. Advantages of nanocrystalline materials are superior phase homogeneity, increased hardness and strength, superior sinterability and new microstructures leading to unique mechanical, electrical, dielectric, magnetic, optical and catalytic properties.

Recently, research on the preparation of nanopowders with superior characteristics is one of the major fields in materials processing technology [2–4]. The coarse-grained powders synthesized using the conventional solid-state route has the disadvantages of larger particle size, high temperature prolonged processing, and relatively lower purity.

Hafnium based perovskite ceramics are rarely studied refractory oxides, while having tremendous applications in electronic materials research and industry. The perovskite structured $BaHfO_3$, $SrHfO_3$ and other alkaline earth hafnates have been well known as high melting temperature materials [5,6]. $BaHfO_3$ doped with Yttrium has been reported as an interesting compound for their applications in fuel cells [7]. $BaHfO_3$ is also reported as promising material for their potential applications as dielectrics for memory applications [8]. Barium hafnate compounds doped with various dopants such as Ce, Yb, Eu, etc., are reported as good luminescent materials [9,10] and good scintillating materials for their potential impact in high-energy nuclear medical applications [11,12]. It was also reported that $BaHfO_3$ could be used as an electrode for arc discharge lamp [13] and materials for humidity sensors [14]. In some of our earlier communications we have reported the new hafnium based double perovskite ceramic material, for their possible applications as a novel substrate for superconductor thin films [15,16].

In all the above references on hafnium-based perovskites, the powder was synthesized through the conventional solid-state reaction method where the particles were of many micron

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sizes. One of the major difficulties in the studies of Hafnium based perovskites is their high processing temperature and high cost of Hafnium oxide. In the earlier reports for the synthesis of phase pure $BaHfO_3$ requires prolonged calcinations at a temperature of about 1300 °C [11]. Also it was reported that $BaHfO_3$ was sintered to high density at a temperature of about 1850 °C for a long duration of 6–12 h in hydrogen atmosphere [10]. Solution synthesis technique offers improved phase homogeneity than that of the conventional solid state ceramic route. Zhou et al. [17] reported the synthesis of $BaHfO_3$ by oxalate method in which phase pure $BaHfO_3$ was obtained only after annealing the precursor to about 800 °C. Combustion synthesis technique offers an easy and cost effective method for the synthesis of nanostructured materials [18]. Different approach of combustion synthesis using different fuel, oxidizers and complexing agents were also reported [19–21]. In all the combustion synthesis technique thus reported requires calcination of the precursors obtained after combustion for phase formation. Recently a modified auto-igniting combustion synthesis technique which employs citric acid as complexing agent and ammonia as fuel was reported as a better method for the synthesis of nanomaterials [22,23]. This method requires no calcination step since phase pure materials are obtained directly after combustion. We have already reported that the sinterability of ABO_3 perovskites based on zirconates prepared by the auto-igniting combustion technique shows improved sinterability with a reduction of sintering temperature of about 150–200 °C, with a reduced sintering time of 2–3 h [24–26]. This may be due to the varying particle size and morphology of the nanomaterials prepared by the combustion technique [27]. In the present work, we are reporting the synthesis, characterization, sintering behavior and dielectric properties of nanocrystalline $BaHfO_3$ synthesized through the modified single step combustion technique.

2. Experimental

In the present study, a modified auto-igniting combustion technique was used for the synthesis of nanoparticles of $BaHfO_3$. In a typical synthesis, aqueous solution containing ions of Ba and Hf was prepared by dissolving stoichiometric amount of high purity, $Ba(NO_3)_2$ and $HfCl_4$ (99%) in double distilled water (200 mL) in a glass beaker. Citric acid (99%) was then added to the solution containing Ba and Hf ions. Amount of citric acid was calculated based on total valence of the oxidizing and the reducing agents for maximum release of energy during combustion [22,23]. Oxidant/fuel ratio of the system was adjusted by adding nitric acid and ammonium hydroxide; and the ratio was kept at unity. The solution containing the precursor mixture at a pH of ~7.0 was heated using a hot plate at ~250 °C in a ventilated fume hood. The solution boils on heating and undergoes dehydration accompanied by foam. The foam then ignites by itself on persistent heating giving voluminous and fluffy product of combustion. The combustion product was subsequently characterized as single-phase nanocrystals of $BaHfO_3$.

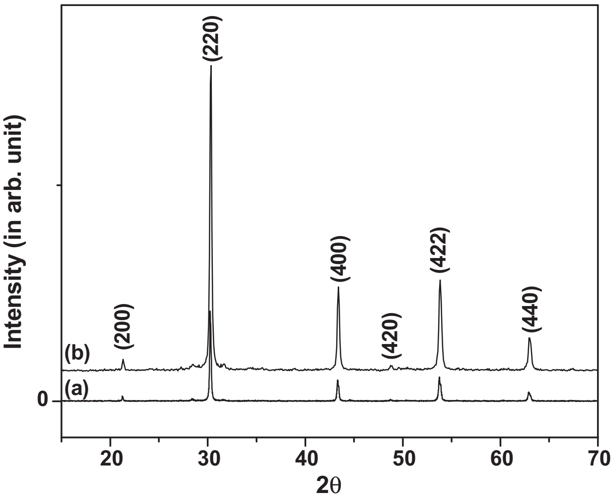

Fig. 1. XRD patterns of $BaHfO_3$.

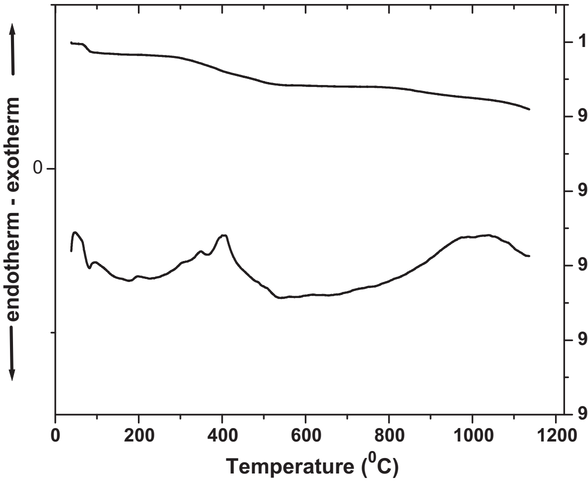

Fig. 2. DTA–TGA curves of $BaHfO_3$.

Structure of the as-prepared powder was examined by powder X-ray diffraction (XRD) technique using an X-ray diffractometer (Model Bruker D-8) with Nickel filtered CuK_α radiation. The differential thermal analysis (DTA) and thermo gravimetric analyses (TGA) were carried out using Perkin-Elmer TG/DT thermal analyzer in the range 30–1000 °C at a heating rate of 20 °C/min in nitrogen atmosphere. The infrared (IR) spectra of the samples were recorded in the range 400–4000 cm^{-1} on a Thermo-Nicolet Avatar 370 Fourier Transform Infrared (FTIR)

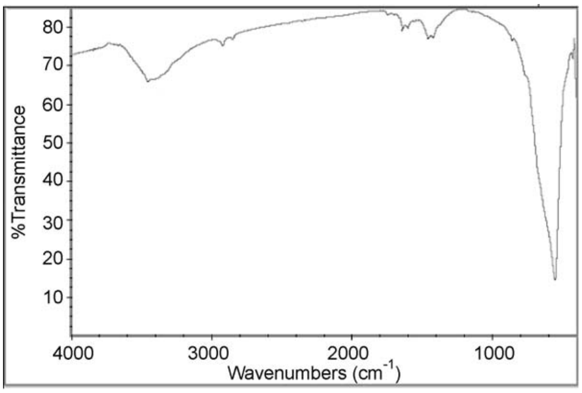

Fig. 3. FT-IR spectra of $BaHfO_3$.

Spectrometer using KBr pellet method. Particulate properties of the combustion product were examined using transmission electron microscopy (Model: JEOL JEM 1011) operating at 200 kV. The samples for Transmission Electron Microscope (TEM) were prepared by ultrasonically dispersing the powder in methanol and allowing a drop of this to dry on a carbon-coated copper grid.

To study the sinterability of the nanoparticles obtained by the present combustion method, the as-prepared $BaHfO_3$ nanoparticles were mixed with 5% polyvinyl alcohol and pressed in the form of cylindrical pellet of 14 mm diameter and ~2 mm thickness at a pressure about 350 MPa using a hydraulic press. The pellet was then sintered at 1650 °C for 2 h. The theoretical densities of the $BaHfO_3$ were calculated from the lattice constants and sintered density was calculated following Archimedes method. The surface morphology of the sintered samples was examined using scanning electron microscopy (SEM, Model-JEOL JSM 5610 LV). For low frequency dielectric studies the pellets were made in the form of a disc capacitor with the specimen as the dielectric medium. Both the flat surfaces of the sintered pellet were polished and then electroded by applying silver paste. The capacitance of the

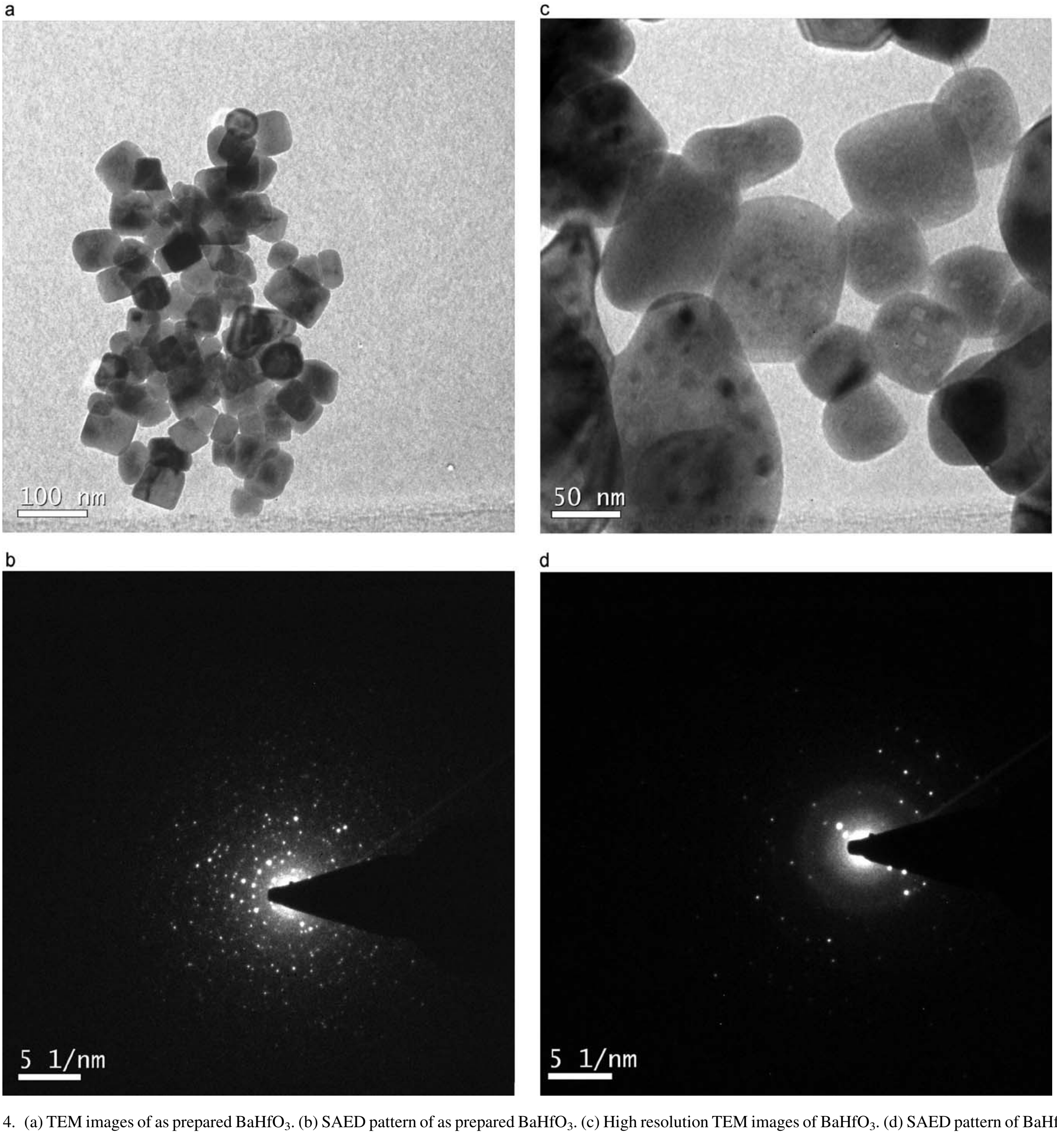

Fig. 4. (a) TEM images of as prepared $BaHfO_3$. (b) SAED pattern of as prepared $BaHfO_3$. (c) High resolution TEM images of $BaHfO_3$. (d) SAED pattern of $BaHfO_3$.

sample was measured using an LCR meter (Hioki-3532-50 LCR HiTester) in the frequency range 100 Hz–5 MHz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the $BaHfO_3$ nanopowders obtained by the present combustion synthesis. Considerable increase in crystallinity of the samples was observed on annealing at 600 °C for h as indicated in Fig. 1(b). In the present combustion synthesis, the phase formation occurs in a very short duration of combustion of the order of about 10 s. This short duration may be the reason for the considerable increase in crystallinity during annealing. All the peaks including the minor one are indexed for the cubic structure (*Pm*3*m*) and they agree well with the reported standard value (JCPDS 24-0102). The crystallite size of the combustion product calculated from full-width-half-maximum (FWHM) using Scherrer formula for the major (2 2 0) plane in Fig. 1(a) is ~15 nm. It may be noted that a single phase $BaHfO_3$ could be obtained through solid state reaction route only after prolonged calcination of the reaction mixture at 1300 °C for many hours with multiple intermediate grindings. In the combustion processes reported for the preparation of nanocrystals of some other ceramic oxides, EDTA, polyvinyl alcohol, etc., were used as complexing agent and ammonia and urea as fuels [19,20]. In these cases prolonged calcinations of the as-prepared powder at temperatures above 600 °C was required to obtain a phase pure sample. In the present auto-igniting combustion method which uses citric acid as complexing agent and ammonia as fuel, we are able to prepare phase pure nanopowders of $BaHfO_3$ in a single step combustion without any calcination step. Also we have used Hafnium oxy-chloride as a starting material for the synthesis of $BaHfO_3$, which is relatively inexpensive than that of hafnium oxide, which are being used as a staring material in the solid state synthesis of $BaHfO_3$. The current method offers an easy, cost effective and time saving method for the preparation of high quality nanopowders of $BaHfO_3$.

Fig. 2 shows the DTA–TGA curves of as prepared $BaHfO_3$ obtained directly after combustion. A small weight loss of about 1% was observed in the TGA curve at about 100 °C which is due to the adsorbed moisture present in materials due to the ultra fine nature of the as prepared material. A small weight loss of >1% was observed in the TGA curve in the range 400 °C, which is due to the presence of traces of nitrates or ammonia in the as prepared powder. There after no considerable weight change was observed on the TGA curve. The variation in DTA curves is in good agreement with that of TGA curve which implies that the phase formation is complete with in the combustion itself and there is no need of any further calcination and is in good agreement with that of XRD results.

Fig. 3 shows the FT-IR spectra of the as prepared $BaHfO_3$. The bands in FT-IR spectra are assigned mainly on the basis of vibrations of HfO_6 octahedra. The IR active $\gamma_3(F_{1u})$ asymmetric stretching mode of HfO_6 octahedra is observed as a strong absorption band at 565 cm^{-1}. The weak bands at 858 cm^{-1} are due to the Raman active symmetric stretching $\gamma_1(A_{1g})$ mode of HfO_6 octahedra [28,29]. The strong absorption band in the region 3000–3600 cm^{-1} is due to the symmetric stretching $\gamma_1(A_1)$ mode and asymmetric stretching γ_3 (F2) modes of NH^{4+} ions in addition to the water adsorbed during pelletization. The bands at 1630 cm^{-1} are due to the γ_2(E) bending modes of NH^{4+} ions. This corroborates the XRD and thermal analysis result that the combustion is complete and no considerable organic matter is present in the sample.

The transmission electron microscopy (TEM) studies on the powder morphology of the as-prepared $BaHfO_3$ nanopowder obtained by the combustion synthesis showed that the nanoparticles are of submicron size 20–50 nm as shown in Fig. 4a .The measured nanocrystalline grains are in the range 20–50 nm with a mean size of 35 nm. The corresponding selected area electron diffraction pattern is also showed in the Fig. 4b. The particles are of regular cuboidal shape with sharp grain boundaries. Individual crystallites in the agglomerates appear well bonded with very few voids in between. The ring nature of the Electron Diffraction Pattern is indicative of the poly crystalline nature of the crystallites, but the spotty nature of the SAD pattern in figure can be due to the fact that the finer crystallites having related orientations are agglomerated together resulting in a limited set of orientations. For a better understanding, magnified TEM image of some selected crystallites are taken and is shown in Fig. 4c, the corresponding SAED pattern in Fig. 4d. The related orientations of the crystallites can be clearly seen from SAED pattern.

The sintering behavior of the nanocrystals of $BaHfO_3$ powders synthesized through the present combustion route was studied. The relative green density of the specimen used for the sintering study was ~55%. A sintered density of about 95% of the theoretical density was obtained on sintering the compacted specimen at 1650 °C for 2 h. Generally micron sized $BaHfO_3$ powder requires special sintering conditions along with very high sintering temperature and very long duration of heating, for better densification [10]. In our present work, the particles are of cuboidal shape having size in the range 20–50 nm. This high sintered density and the reduced temperature–time schedule can be attributed to the enhanced kinetics due to the small degree of agglomeration, its grain morphology and ultra-fine nature of $BaHfO_3$ prepared in the present study. No

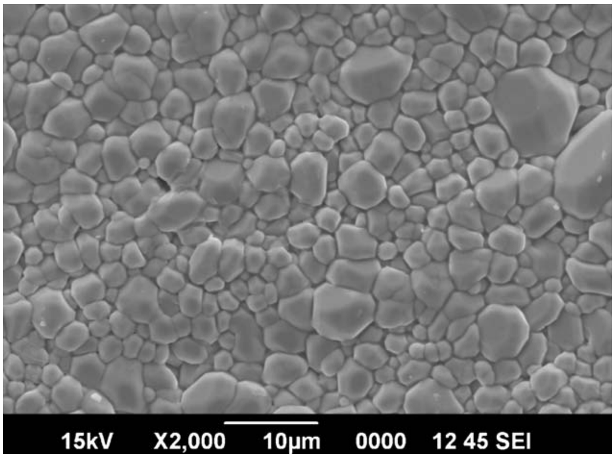

Fig. 5. SEM images of $BaHfO_3$.

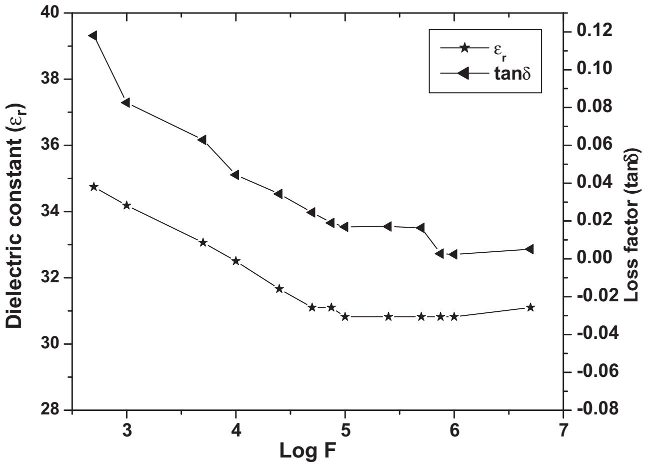

Fig. 6. Dielectric response of $BaHfO_3$.

cracks or pores were observed on the surface. It is clear from the micrographs that densification was achieved without significant microstructural coarsening. Average grain size determined from the SEM micrographs is ~4 μm (Fig. 5).

The dielectric behavior of sintered samples of $BaHfO_3$ nanocrystals is shown in Fig. 6.Thevariation of dielectric constant with frequency is almost similar with that reported earlier for pellets prepared from micron-sized particles [30]. The dielectric constant (ε_r) and loss tangent (tan δ) for1 MHz are about 30.8 and 2.3×10^{-3}, respectively.

4. Conclusions

Barium hafnate and strontium hafnate are complex perovskite ceramic material, of the family $ABO_{3,}$ were synthesized in nanoscale using an auto-igniting combustion of a precursor solution containing metal ions, oxidant, and a fuel. Phase-purity and particulate properties of the as-prepared powder were examined using X-ray diffraction, differential thermal and thermo gravimetric analyses, Fourier-transform of infrared spectroscopy, scanning electron microscopy, transmission electron microscopy and electron diffraction techniques. The as-prepared powder was single phase, crystalline, and composed of particles of average size ~35 nm. The $BaHfO_3$ nanocrystals were sintered to 97% of its theoretical density on heating at 1600 °C for 4 h.

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