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A study on the synthesis of (Ba,Ca)(Ti,Zr)O_3 nano powders using Pechini polymeric precursor method

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Abstract

Pechini polymeric precursor method was successfully used to synthesize $(Ba_{0.95}Ca_{0.05})(Ti_{0.85}Zr_{0.15})O_3$ nano powders. The results of TG/DTA, XRD and IR analyses showed that by heating the precursor between 490 °C and 580 °C, an intermediate phase with possible composition of $(Ba,Ca)_2(Ti,Zr)_2O_5CO_3$ was formed. Between 580 °C and 700 °C, the intermediate phase transformed to a crystalline solid solution by decarbonation reaction. The transformation completed at 700 °C. Nano-sized powders with equivalent sphere diameters about 72 nm were obtained by calcination of the precursor at 700 °C for 4 h. The ceramics sintered at 1300 °C for 2 h can reach about 95% theoretical density and the peak dielectric constant is 15,000 at 70 °C.

Keywords: Pechini; Polymeric precursor; Perovskites; Nano powder; BCTZ

1. Introduction

Barium titanate with perovskite structure is an important electronic ceramic because of its excellent properties, which are applied to several electronic components extensively. In particular, the barium and titanium sites of perovskite structure can be substituted partially or completely by other cations, such as Ca^{2+}, Sr^{2+}, Zr^{4+} etc., to change its electrical properties [1,2]. These substitutions offer possibilities in many applications, which require specific dielectric, piezoelectric, semiconductive and optical properties. One of the major applications of barium titanate is ceramic capacitors with different types. The most important type is chip capacitor, especially multi-layer ceramic capacitor (MLCC). This is due to the fast development of digital electronic devices. MLCC has good dielectric properties, lower equivalent series resistance (ESR) and potential to provide high capacitance with the introduction of advanced multi-layers technology. Meanwhile, the chip-type structure makes it appropriate in surface mount assembly. The applications of MLCC even have gradually overlapped the range of Tantalum capacitor [3].

In recent years, the main development of MLCC technology concentrated on the making of thinner dielectric (e.g., <1 μm) so as to increase the capacitance per unit volume. In order to achieve this goal, the raw materials must fulfill the following conditions: (1) smaller particle size, (2) homogenous composition, (3) effective particle packing in green body, and (4) smaller grain size of the sintered ceramics. When the above requirements are achieved, the thinned dielectric might be able to achieve good dielectric strength and long life.

Among the MLCCs, the Y5V specification (working temperature in the range of −30 °C to 85 °C, $\Delta C/C_{25\,^{\circ}\mathrm{C}} = -82$ to 22%) has the most extensive applications because its dielectric constant is larger than 10,000 at room temperature. However, the dielectric constant of pure barium titanate is a function of temperature with a peak value at 130 °C, the Curie temperature. The temperature dependent characteristic of pure barium titanate cannot meet Y5V specifications. Therefore, it was modified by partially substituting Ba^{2+} by Ca^{2+} and Ti^{4+} by Zr^{4+} in the perovskite structure. By doing this, the peak value can be shifted to room temperature and the temperature characteristic can be tempered to let its dielectric constant meet Y5V specifications [4,5].

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In 1967, Pechini announced a patent, in which he used citric acid as chelating agent to catch cations, which were dissolved in ethylene glycol solution, then heated the solution to promote esterization and polymerization to form a resin-like gel. Finally, the resin was calcined at certain higher temperatures to form expected powders [6]. Using this method, Pechini has successfully synthesized $BaTiO_3$, $BaZrO_3$ and $BaNb_2O_6$ ceramic powders. This process is named as Pechini method or Pechini process. Similar processes have been developed by other scientists later, thus it is also named as polymeric precursor method [7,8].

Pechini process can be used to synthesize single phase compounds [9] and has extended to compounds of solid solution form [10]. Traditionally, commercial ceramic powders are prepared using solid-state reaction process. The disadvantages of solid-state method include coarser particle size, poor homogeneity and irregular morphology. These disadvantages make solid-state method difficult to fulfill the requirements for advanced ceramic capacitors in achieving thinner dielectrics for higher capacitance applications. Other wet synthesis processes, such as sol–gel [11], hydrothermal [12], co-precipitation [13], have been studied in the preparation of barium titanate powders. Very fine powders can be produced using these methods, however, to make thinner dielectrics from these powders some difficulties still exist. The polymeric precursor method not only can produce nano-scaled powder, most specifically, the precursor itself has a resin-like structure with a proper viscosity, which makes it easily forming thin films on substrate by general coating process. Thus polymeric precursor method has better potential in the manufacturing of thin film dielectrics. This study is using Pechini polymeric precursor process to synthesize $(Ba_{0.95}Ca_{0.05})(Ti_{0.85}Zr_{0.15})O_3$ (BCTZ) nano-powders, the reaction mechanism of the solid solution system is investigated, which will be further applied in the preparation of BCTZ thin films.

2. Experimental

First, 28.89 g (0.085 mol) of tetra-*n*-butyl titanate $[Ti(OC_4H_9)_4]$ and 5.75 g (0.015 mol) of tetra-*n*-butyl zirconate $[Zr(OC_4H_9)_4]$ were mixed at room temperature. The solution was then added to a solvent of weight 100 g and 1:4 mole ratio of citric acid $[C_3H_4(COOH)_3]$ and ethylene glycol $[C_2H_4(OH)_2]$. The mixture was heated with continuous stirring at 60 °C. During heating, 18.75 g (0.095 mol) $BaCO_3$ and 0.5 g (0.005 mol) $CaCO_3$ were added gradually to the solution until the solution became transparent, which meant complete dissolving. The final solution was an atomic level state of mixing of Ba, Ca, Ti, Zr at the ratio of 0.95:0.05:0.85:0.15, and was used as the raw material to prepare nano-powders.

The solution was moved to an oven and heated at 140 °C for 2 h to promote esterization and polymerization and a light yellow, transparent and viscous resin was obtained. The resin was put in an aluminum oxide crucible and heated at 300 °C for 4 h to decompose the resin. Dark brown powders were obtained. The powder was further calcined in an electrical furnace at higher temperatures for 4 h to prepare BCTZ powders.

The calcined powders were crushed and dispersed by ball milling with 2 mm zirconia beads in ethanol for 8 h. Then 10 wt% of PVB (polyvinyl butyral) based on BCTZ powder was added to the dispersed BCTZ slurry and the stirring was kept for 2 h. The mixed slurry was cast by doctor blade and dried to 100 μm thick films. The dried films were stacked and pressed at 48 MPa and 80 °C for 30 min to form green plates of 1 cm^2 area and 1 mm thickness. The greens were sintered by an electrical furnace at temperatures from 1100 °C to 1300 °C for 2 h with ramp temperature of 5 °C/min. Both faces of sintered ceramic plates were painted with silver paste then fired at 800 °C for 20 min to form parallel plate capacitors for dielectric analysis.

3. Characterization

The TG/DTA (Netzsch STA409) analysis up to 1000 °C in air was used to investigate the weight loss and endothermic/exothermic reactions during calcination of the heat-treated resins. The heating rate was set at 10 °C/min.

Computer-interfaced X-ray powder diffraction (XRD) with $CuK_{\alpha1}$ radiation ($\lambda = 1.5406$ Å) (Siemens D5000) was used to identify the crystalline phases. The scanning angle (2θ) was from 20° to 80° and the power of 40 kV/30 mA was applied.

The specific surface area of the powders was measured by BET method. The powders were dried in a vacuum chest for 24 h, then injected with nitrogen and heated to 200 °C for 4 h to ensure complete moisture removal. A surface area analyzer (Micromeritics Gemini 2360) was used in this measurement. The equivalent sphere diameter is calculated by Eq. (1),

$$d = \frac{k}{\rho \times A} \tag{1}$$

d is the particle size (μm), k is the shape factor (shape factor is 6 as the particle is assumed to be spherical), ρ is the density (g/cm^3) and A is the specific surface area (m^2/g).

Infrared spectra of powders were recorded in the 400–4000 cm^{-1} range using a FT/IR Spectrometer (JASCO's FT/IR-410Plus) by preparing KBr (Merck for spectroscopy) pellets (5 wt% sample) to investigate the bonding of precursors and calcined powders.

The morphological features of the BCTZ powders were observed using a scanning electron microscope (SEM; Philips XL-40FEG).

The density of sintered ceramic was measured by Archimedes's method. The capacitance was measured by a HP4284A LCR meter at 1 KHz, 1 Vrms. The dielectric constant is calculated by Eq. (2).

$$K = \frac{C \times t}{A \times \varepsilon_0} \tag{2}$$

K is the dielectric constant, C is the capacitance (F), t is the dielectric thickness (m), A is the area (m^2) and ε_0 is the vacuum permittivity (8.85×10^{-12} F/m).

4. Results and discussion

Fig. 1 shows the TG/DTA curves of BCTZ precursor after preheating at 300 °C. A minor weight loss from room temperature to about 200 °C can be seen and is associated with the weak endothermic peak (mark 1) on TG/DTA curve. This should be the dehydration reaction of surface water [14]. Although the precursor had been pretreated at 300 °C, some moisture may be re-adsorbed during cooling down to room temperature because of the high surface area of the precursor after heat treatment.

The first exothermic peak appears between 300 °C and 380 °C (DTA curve, mark 2). This probably is the oxidation reaction or combustion of the organics in the precursor as evidenced by the significant weight loss starts at 300 °C. The preheating treatment at 300 °C may have some dehydration and de-carboxylation to the resin [14], however, carbon still exists in the organic compound and can be burned off only above 300 °C. The precursor after preheating is amorphous as being shown in Fig. 2a, and is maintained as amorphous even at 525 °C although some peaks are appearing (Fig. 2b–e). From the IR spectra, it can be seen that the precursor below 200 °C (Fig. 3a and b) show that the asymmetric(as) and symmetric(s) absorption peaks of carboxylic group –COO$^-$ are at 1548 cm^{-1} and 1382 cm^{-1}, respectively. The wave number difference $\Delta\nu$ ($\Delta\nu = \nu_{as}(\text{–COO}^-) - \nu_s(\text{–COO}^-) = 1548 - 1382$) is 166 cm^{-1}, which means that the chelation between the cations and the carboxylic group belongs to the bridging type. When the temperature rises to 350 °C, the peaks shift to 1531 cm^{-1} and 1373 cm^{-1} (Fig. 3c), i.e., $\Delta\nu = 158$ cm^{-1}, which means the chelation has become ionic type [15].

The second exothermic peak appears between 380 °C and 525 °C (mark 3 in Fig. 1). From Fig. 2d and e, it can be shown that an intermediate crystalline phase starts to appear at 490 °C, indicating the organic precursor, besides the foregoing de-carboxylation reaction, starts to form some crystalline phase, although only a fraction of crystalline phases occur, by an exothermic reaction. The IR spectra in Fig. 3e shows the appearance of CO_3^{2-} at 490 °C. Kumar et al. [16] reported that a $BaTi_2O_5CO_3$ intermediate phase exists temporarily between 500 °C and 620 °C in the synthesis of barium titanate using citric acid sol–gel method. Similarly, it can be reasonably assumed that an intermediate phase with a probable composition of $(Ba,Ca)_2(Ti,Zr)_2O_5CO_3$ may also start to form.

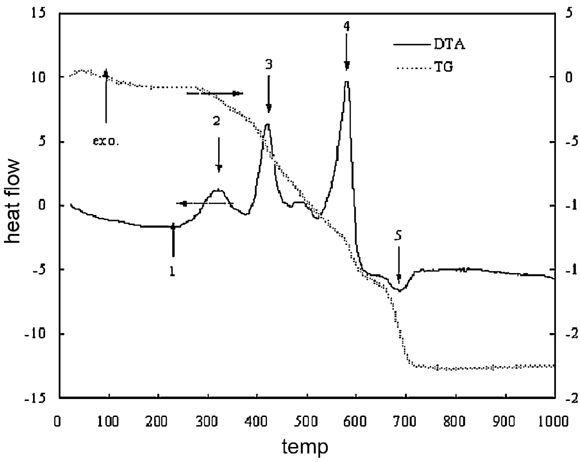

Fig. 1. TG/DTA curves of the BCTZ precursor.

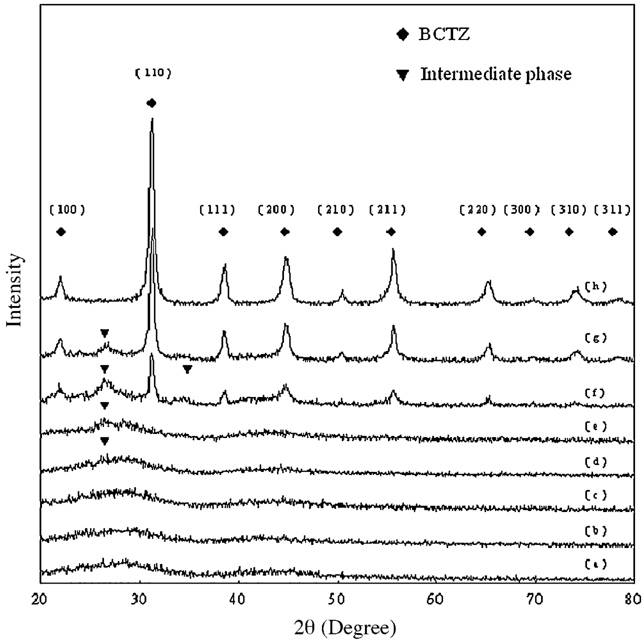

Fig. 2. XRD patterns of (a) BCTZ preheated precursor; calcined at (b) 200 °C, (c) 422 °C, (d) 490 °C, (e) 525 °C, (f) 580 °C, (g) 600 °C, and (h) 700 °C.

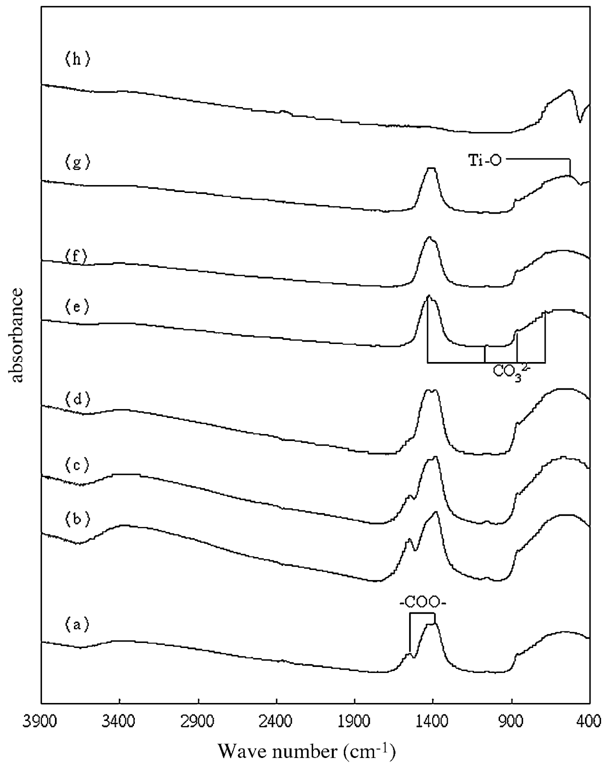

Fig. 3. IR spectra of (a) BCTZ preheated precursor; calcined at (b) 200 °C, (c) 350 °C, (d) 422 °C, (e) 490 °C, (f) 525 °C, (g) 580 °C, and (h) 700 °C.

The third exothermic peak appears at 580 °C (Fig. 1, mark 4). By comparing the XRD pattern of Fig. 2e and f, it can be shown that the intermediate phase, which starts to appear at 490 °C, reaches its maximum of formation by further combustion of hydrocarbons, simultaneously with some of BCTZ formed. The IR spectra of Fig. 3g shows that Ti–O bonding appears at 580 °C. These two phases co-exist between 580 °C and 600 °C as shown in Fig. 2g.

The final thermal reaction at about 690 °C is an endothermic type (Fig. 1, mark 5). This endothermic reaction probably is a combination of the de-carbonation of intermediate phase and the followed particle growth or increases of crystallinity of BCTZ. Comparing Fig. 2f and g of XRD, it can be seen that BCTZ phase starts to appear at 580 °C and the peak of (1 1 0) plane becomes stronger with the increase of temperatures. While the peak of the intermediate phase is the strongest at 580 °C, but decreases rapidly above 600 °C, obviously because of the formation of BCTZ by de-carbonation of intermediate phase. The previous exothermic reaction at 580 °C (mark 4) is the transformation of carboxylic compounds to carbonate, i.e., the intermediate phase. At about 600 °C, the reaction turns to endothermic and reaches a maximum at about 690 °C (Fig. 1, mark 5). Higher than 690 °C, the TG curve becomes horizontal, indicating the end of transformation. Fig. 2h shows that at 690 °C the intermediate phase has completely transformed to BCTZ and the continuous endothermic reaction probably is due to the increase in crystallinity. The IR spectra in Fig. 3h also shows that CO_3^{2-} bond disappears completely at 700 °C, in accordance with TG/DTA and XRD analyses.

Table 1 lists the equivalent sphere diameters of synthesized powders calculated by Eq. (1) from the specific surface area data. The powders calcined below 900 °C are all nano-sized. The particles grow slowly between 600 °C and 700 °C during the formation of BCTZ from intermediate phase. Particle growth accelerates above 700 °C after the transformation is completed. The SEM pictures in Fig. 4 shows the morphology of BCTZ powders calcined at 700 °C and 900 °C. It can be seen that particles are generally in spherical shape and the visually estimated size is close to the results calculated from specific surface area data. These results show that nano-sized BCTZ powder can be synthesized successfully by Pechini polymeric precursor method at temperature between 700 °C and 800 °C.

Table 1
Specific surface area and equivalent diameter of BCTZ powders calcined at different temperatures.

Calcination temperature (°C)	BET specific surface area (m^2/g)	Equivalent sphere diameter (nm)
600	14.9005	69.4
700	14.3142	72.3
800	10.6462	97.2
900	8.0341	128.8

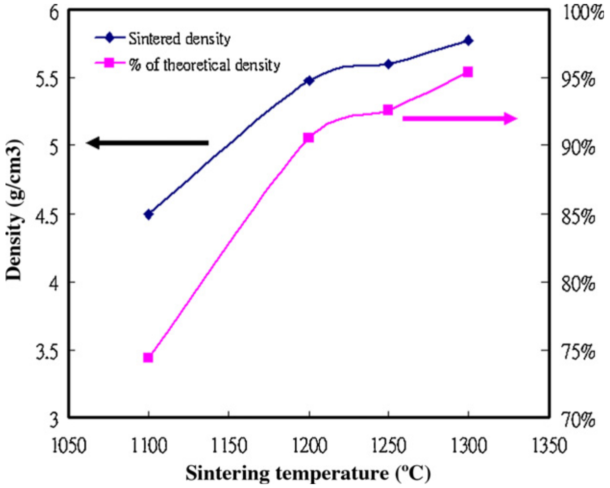

Fig. 5. Effect of sintering temperature on density for BCTZ ceramics.

The theoretical density of BCTZ calculated with lattice parameters obtained from XRD patterns is 6.05 g/cm^3. The sintered densities of ceramics are shown in Fig. 5. It can be seen that below 1250 °C, the sintered density is less than 93% of theoretical value. Raising to 1300 °C, the sintered density can reach 95% of theoretical value, however, high sintering temperature also resulted in pore growth as shown in Fig. 6. The dielectric properties of the three sintered ceramics are shown in Fig. 7. The peak permittivities all appear at about 70 °C. Obviously, this is due to 15% substitution of Zr^{4+} for Ti^{4+} in $BaTiO_3$, similar results were reported of 13% substitution of Zr^{4+} for Ti^{4+} [17]. The peak dielectric constant is about 15000 for the ceramics sintered at 1300 °C, which is close to commercial level. By changing the Zr content of BCTZ powder, the peak value of

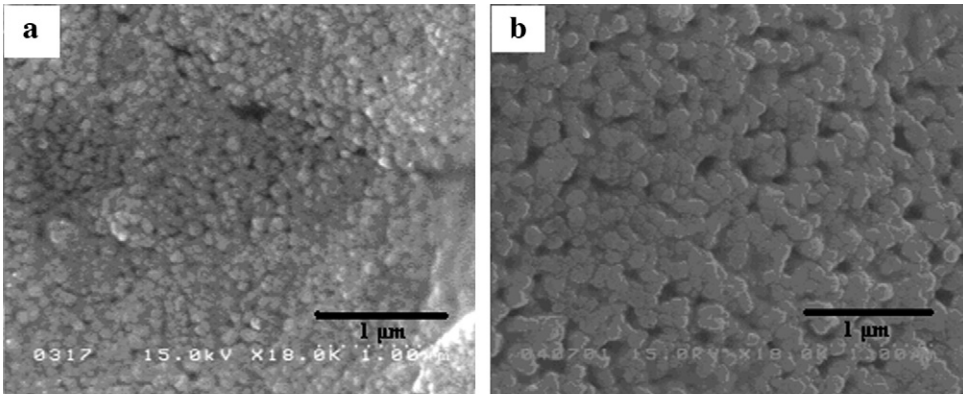

Fig. 4. SEM micrographs of BCTZ powders calcined at (a)700 °C and (b)900 °C for 4 h.

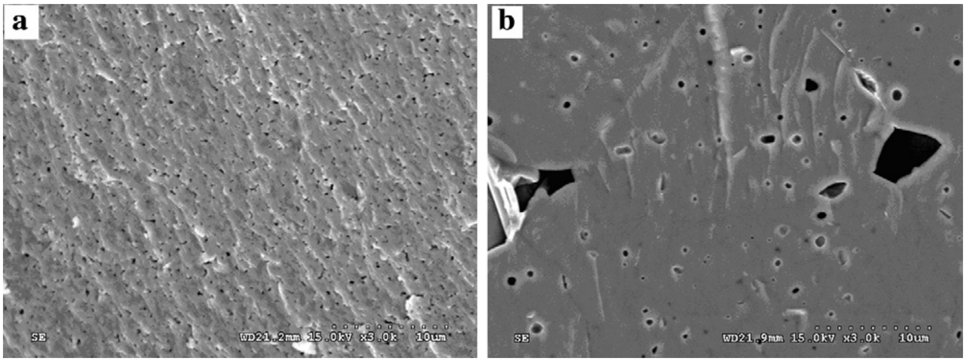

Fig. 6. SEM micrographs of fracture cross-section of BCTZ ceramics sintered at (a) 1200 °C and (b) 1300 °C for 2 h.

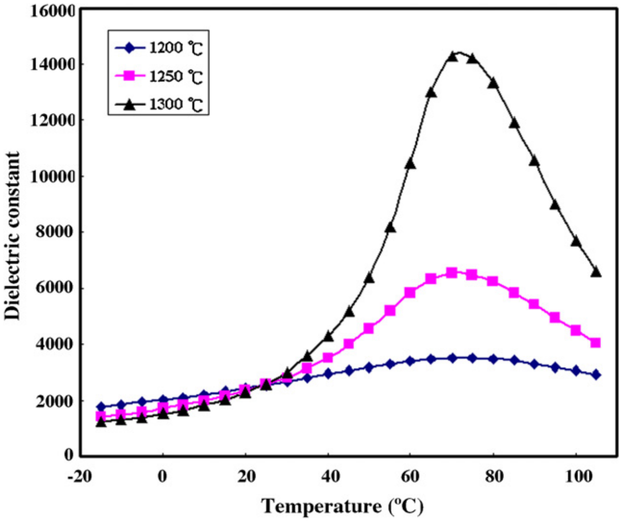

Fig. 7. Temperature dependence of dielectric constant of BCTZ ceramics sintered from 1200 °C to 1300 °C for 2 h.

BCTZ powder can be preferentially shifted to meet commercial requirements for specific temperature.

5. Conclusions

In this study, Pechini polymeric precursor method was used to synthesize BCTZ powders. The characteristics of the precursor during the process of heating were analyzed by TG/DTA, XRD and IR, the results showed that a crystalline intermediate phase probably of the composition $(Ba,Ca)_2(Ti,Zr)_2O_5CO_3$ formed between 490 °C and 580 °C. The crystalline BCTZ phase began to form at 580 °C from the intermediate phase by de-carbonation and completed the transformation at 700 °C. By calcination of the precursor at 700 °C for 4 h, nano-sized powders with the equivalent sphere diameter of 72 nm and the composition of $(Ba_{0.95}Ca_{0.05})(Ti_{0.85}Zr_{0.15})O_3$ can be synthesized successfully. The ceramics sintered at 1300 °C for 2 h shows a peak dielectric constant of 15,000 at 70 °C.

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