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Preparation of barium titanate ultrafine powders from a monomeric metallo-organic precursor by combined solid-state polymerisation and pyrolysis

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A recipe has been elaborated for preparing barium titanate ($BaTiO_3$) particles in a nucleation route which is mediated by thermal decomposition of polymeric barium titanium methacrylate. Adjustment of particle size d in the range from 10 nm to 1.5 μm is easily done by choosing appropriate reaction temperatures and tempering atmospheres. In particular, doping with paramagnetic probe ions such as Mn^{2+}, Gd^{3+} or Cr^{3+} can be readily accomplished by just adding the corresponding metal acetates to the monomeric precursor. In addition to well approved standard techniques such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and differential scanning calorimetry (DSC), the complementary spectroscopic methods electron paramagnetic resonance (EPR), nuclear magnetic resonance (NMR), X-ray absorption near edge structure (XANES) and FT-Raman are applied to characterise the micro- and nanocrystalline $BaTiO_3$ powders prepared and to study the phase transition behaviour in dependence on the mean particle size. In contrast to expectation from literature, the dimensionality effect does not manifest itself in a temperature shift of the ferroelectric phase transition but, instead, the tetragonal-to-cubic phase transition is smeared out at reduced particle size and an increasing tetragonal-to-cubic phase admixture is detected. *© 1999 Kluwer Academic Publishers*

1. Introduction

The perovskite-type $BaTiO_3$ is one of the most important ferroelectric materials. Moreover, flexible ferroelectric ceramic/polymer composite foils are under extensive study as technologically promising integrated-capacitor thin film materials offering both high dielectric permittivity and low loss [1]. To attain thin homogeneous composites relatively small particles had to be used. However, the ferroelectric properties critically depend on the particle size [2, 3] and first heat wave studies of the electric poling and switching behaviour of such ceramic/polymer composites, using the stationary laser intensity modulation method (LIMM) [4] and the thermal pulse method (TP) [5], indeed disclosed critical particle size effects for the latter systems, too. In addition, volume and surface imperfections efficiently co-operate in determining the properties of small ferroelectric particles, even yielding a correlational length below the geometrical dimension [3]. Hence, preparation of perfect ferroelectric particles over a wide size range still represents a relevant task in material science and development.

In this paper, we present a new preparation route for ultrafine $BaTiO_3$ powders and its extensive characterisation, particularly employing, besides common calorimetric, gravimetric, diffractive and microscopic means, several spectroscopic tools which furnish detailed information on local symmetries and size-dependent phase transition behaviour. In such an endeavour we employ Mn^{2+} as probe ions for the application of EPR spectroscopy, which is also an important dopant for preparing materials with a positive temperature coefficient (PTC [6]). Hence, the results of the present study are also of potential relevance in delineating a more detailed idea of the PTC effect and, moreover, in developing optimised PTC devices.

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2. Experimental

2.1. $BaTiO_3$ nanopowder preparation

Different ways of preparing nanocrystalline $BaTiO_3$ particles are known, e.g. by hydrothermal [7], sol-gel [8], microemulsion [9] and gas-condensation processes [10], as well as by metallo-organic precursor pyrolysis (MOPP) [11], hydrolytic decomposition [12] and chemical precipitation from solutions [13, 14]. Notwithstanding the high level attained in the respective preparation a serious disadvantage remains: Either a particular route furnishes particles in the 10 nm size range, with only poor possibilities for a straightforward size adjustment, or, alternatively, the preparation method yields sub-micron powders with adjustable mean grain size, however not reaching in the latter case the size range (below 100 nm) which is of interest in a study of dimensionality effects on ferroelectricity. Besides a more efficient size adjustment in the wide range from 10 nm up to about 1.5 μm, our route aims at a homogeneous doping by paramagnetic ions with concentrations ranging from typically 0.05 mol % for EPR measurements up to some mol % for PTC materials.

Our preparation method took part of its pattern from a literature recipe for synthesising nanoferrites [15] and may be described in a dense way by the four reactions:

$$\begin{aligned} &\mathrm{Ba} + \mathrm{Ti(O\text{-}}i\mathrm{C_3H_7)_4} + \mathrm{6CH_2{=}C(CH_3)\text{-}COOH} \\ &\quad \rightarrow \mathrm{BaTi[OOC\text{-}C(CH_3){=}CH_2]_6} + \mathrm{H_2} \\ &\qquad + 4i\text{-}\mathrm{C_3H_7OH} \end{aligned} \tag{1}$$

$$\begin{aligned} &n\mathrm{BaTi[OOC\text{-}C(CH)_3{=}CH_2]_6} \\ &\quad \rightarrow \mathrm{[BaTi(OOC\text{-}C(CH_3)\text{-}CH_2)_6]}_n \end{aligned} \tag{2}$$

$$\begin{aligned} &\mathrm{[BaTi(OOC\text{-}C(CH_3)\text{-}CH_2)_6]}_n \\ &\quad \rightarrow \mathrm{BaCO_3} + \mathrm{TiO_2} + \mathrm{C} + \text{volatiles} \end{aligned} \tag{3}$$

$$\mathrm{BaCO_3} + \mathrm{TiO_2} \rightarrow \mathrm{BaTiO_3} + \mathrm{CO_2} \tag{4}$$

In the first step, barium titanium methacrylate is obtained as a monomeric metallo-organic precursor from metallic barium, titanium(IV)isopropylate and methacrylic acid in boiling methanol. The product (yield 97%) was verified by elemental and thermogravimetric analysis (TGA) as well as by recording the Fourier-transform infrared (FTIR) spectra and X-ray absorption near edge structure (XANES) at the Ti K edge. Measurements by differential scanning calorimetry (DSC) and TGA have shown that reactions (2) and (3) occur simultaneously: solid state polymerisation and concomitant pyrolysis proceed at temperatures above 200 °C. During the pyrolysis step, a char of carbon, C, is formed which burns off in an oxidative atmosphere. The organic residue is turned into various undifferentiated volatile decomposition products. Nucleation and growth of $BaTiO_3$ particles (4) start at about 600 °C, where the temperature and reaction atmosphere determine the resulting particle size. High temperature and oxidative atmosphere tend to produce a large particle size (e.g. 1350 °C and O_2 lead to 1.1 μm mean size) while at lower temperature and under inert atmosphere smaller particles are obtained (e.g. 600 °C and N_2 yield 10 nm particles). It is worth mentioning that in our final preparation route, reactions (2, 3) proceed simultaneously in the heating period (with heating rate 40 K/min) of the high temperature furnace used for the reaction (4). Best powder quality could be attained by combining tempering under oxidative atmosphere with a subsequent one under inert conditions (typically 2 days N_2, 2 hours O_2).

2.2. Characterisation

XANES measurements of the $BaTiO_3$ powder samples were performed at the storage ring of the Center for Advanced Microstructure and Devices (CAMD) in Baton Rouge. It was operated at 1.3 GeV with an average current of about 100 mA. Synchrotron radiation was monochromatised using a vacuum double monochromator of the Lemonnier type, providing a resolution of about 1 eV. All samples were measured as powders which were put onto an adhesive tape.

X-ray diffraction (XRD) patterns of the $BaTiO_3$ powders were taken using a diffractometer (Philips, X-Pert System) with CuK_α radiation.

Scanning electron microscopic (SEM) images were obtained at 30 keV using a JEOL JSM 6600 instrument. The samples were metallised with Au using a Balzers SCD 020 coater.

FT-Raman spectra of the nanopowders with varying particle size were recorded using the Bruker RFS 100 spectrometer. These spectroscopic studies were carried out in the temperature range from -140 °C up to $+140$ °C.

A Bruker ESP 380 EPR spectrometer was used to record the EPR spectra of Mn^{2+} doped $BaTiO_3$ powders both in the X and the Q band (at 9.5 GHz and 34.0 GHz, respectively). The ferroelectric tetragonal-to-cubic phase transition (at about 120 °C) can be clearly inferred from the well-resolved 6-line hyperfine splitting (nuclear spin $I = 5/2$) in the EPR spectrum which is largely smeared out in the tetragonal phase (due to anisotropic fine structure interaction in the powder: electron spin $S = 5/2$).

The ^{137}Ba NMR spectra were measured by means of a Bruker MSL 500 NMR spectrometer (with a d.c. magnetic field of 11.744 T) in the temperature range between 70 °C and 140 °C. Only the central transitions ($m_I = -1/2 \leftrightarrow +1/2$) were investigated which are determined by the quadrupole coupling in second order of perturbation theory. Since line broadening due to the quadrupole interaction is absent in the cubic phase, these measurements allow a sensitive study of the phase transition.

3. Results and discussion

The Ti K XANES spectra of $BaTiO_3$ powders of medium grain size in Fig. 1 reveal a rather good agreement with those shown in literature (e.g., see [16]). In particular, the pronounced differences, occurring between the spectral features taken from the metallo-organic monomeric precursor and the resulting $BaTiO_3$ powders, can provide kinetic information on the $BaTiO_3$ powder formation. Corresponding

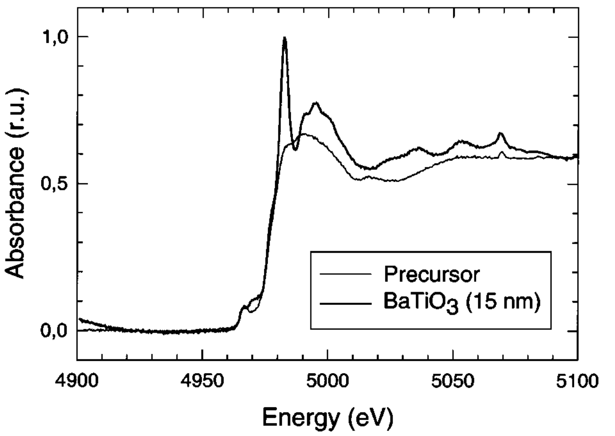

Figure 1 XANES spectra as taken for the monomeric metallo-organic precursor and resulting $BaTiO_3$ powder at the Ti K edge.

time-resolved XANES measurements are under way at the ELSA synchrotron facility of Bonn university.

Fig. 2 shows a SEM image of a resultant $BaTiO_3$ powder with mean particle sizes in the sub-μm region. Particularly for the smaller-grained powders a considerable agglomeration occurs which, however, is removed in the ceramic/polymer composite foil thanks to the powder/monomer dispersion which is prepared prior to polymerisation [5]. Numerous such SEM morphological studies have shown that in the concentration range as applied for the EPR studies (typically 0.05 mol %) doping has no effect on particle morphology.

The (111) XRD peaks of $BaTiO_3$ powders in Fig. 3 reveal for smaller particle sizes an increasing broadening which is accompanied by a shift to a lower scattering angle. For deriving the mean particle size *d* of the $BaTiO_3$ powders, the half-value width of the XRD peak on the (111) face was used in terms of Scherrer's equation [17].

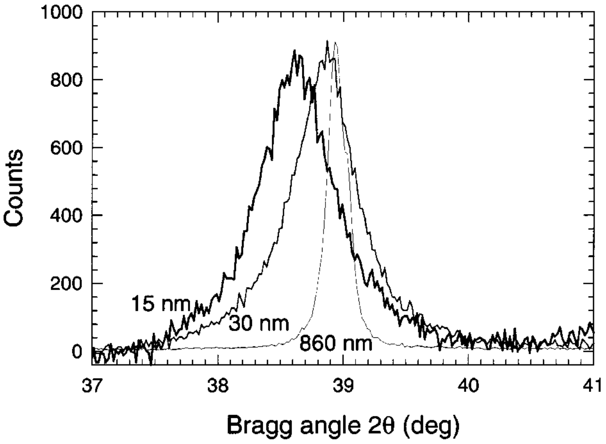

Figure 3 (111) XRD peak of $BaTiO_3$ nanopowders with various mean particle sizes.

In the calculation of d, the effects of mechanical and lattice distortions were then taken into account according to the method of Warren and Averbach [18]. The dependencies of the average particle size on the tempering conditions (cf. Fig. 4) clearly reveal the possibility to adjust the mean particle size by proper choice of tempering temperature and atmosphere. The smaller size in the lower curve in Fig. 4 can be traced back to the char of carbon which tends to cover the growing particles under inert atmosphere.

At an early stage of preparation, besides the characteristic $BaTiO_3$ Raman features in the wavenumber range from 50 to 800 cm^{-1} additional Raman modes were detected such as those occurring in the upper spectrum in Fig. 5 at about 1300 and 1650 cm^{-1}. The latter may be attributed to intermediate sub-phases [19] (cf. upper spectrum of the "distorted" particles in Fig. 5). These distortions could be largely removed by

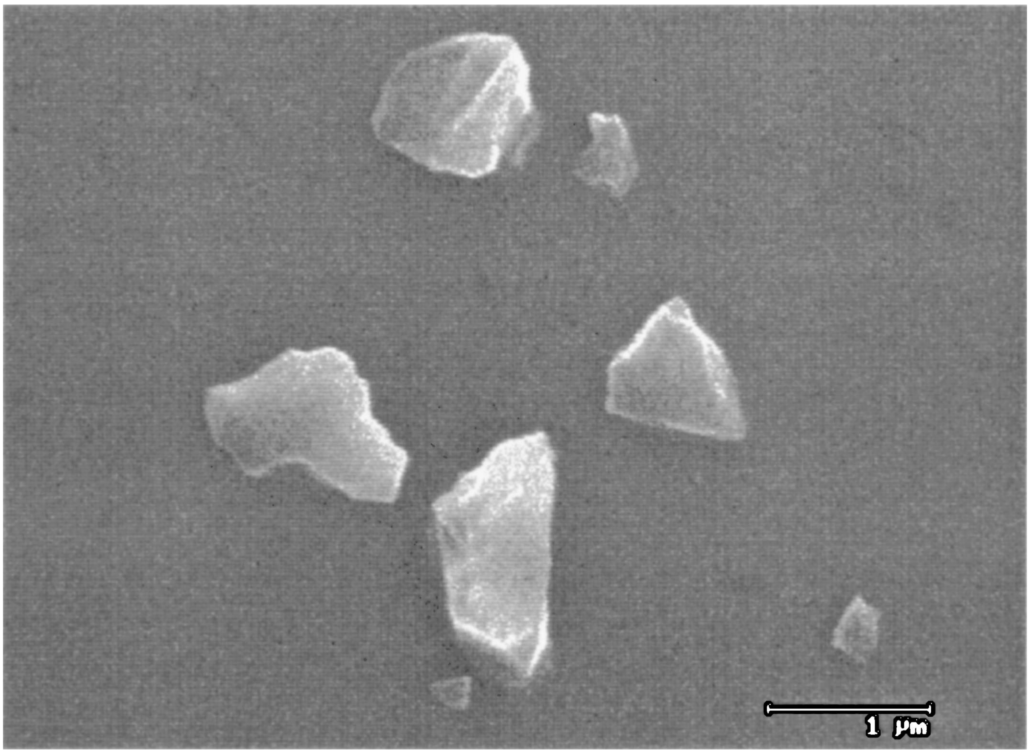

Figure 2 Scanning electron micrograph of Gd^{3+}-doped $BaTiO_3$ particles with a mean size of 860 nm.

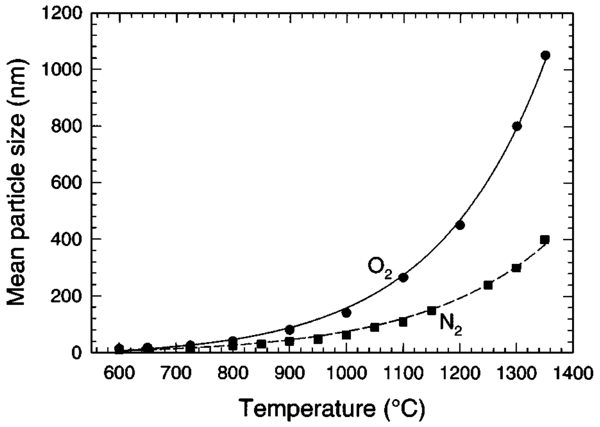

Figure 4 Dependence of the average size d of $BaTiO_3$ particles on tempering conditions (2 days under oxidative atmosphere—O_2, 2 days inert—N_2).

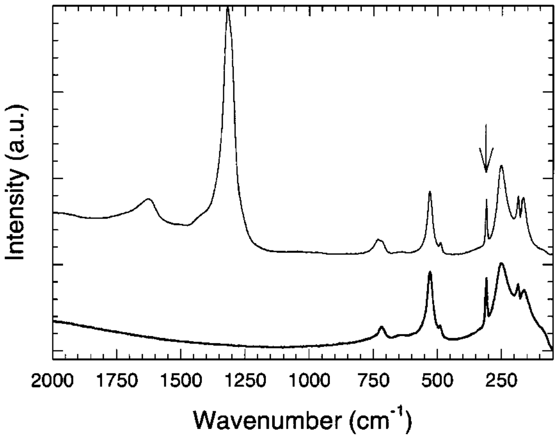

Figure 5 FT-Raman spectra of “distorted” (upper spectrum) and “perfect” $BaTiO_3$-nanoparticles. The “tetragonal” vibration mode at 309 cm^{-1} is indicated by an arrow.

tempering under inert conditions (cf. the lower spectrum in Fig. 5).

$BaTiO_3$ shows a paraelectric-ferroelectric phase transition which may be observed by Raman spectroscopy in the temperature range bridging the ferroelectric transition at a Curie temperature of about 120 °C. In an early study of $BaTiO_3$ bulk systems [20], the characteristic Raman features were found to undergo specific changes at all structural phase transitions (rhombohedral-orthorhombic-tetragonal-cubic). We have found similar spectra for powders of particles with $d > 100$ nm. The specific spectral changes (see the intensity of the “tetragonal” vibration band at 309 cm^{-1} in Fig. 6) reveal a transition behaviour which is increasingly smeared with decreasing particle size, thus confirming a decrease of ferroelectric order at small dimensions. Only a residual “tetragonal” spectrum is left for 15 nm powders (cf. lower part of Fig. 6). The corresponding characteristics for the single crystal ($d = 2$ mm) provides indication of pronounced ferroelectric properties, in particular with respect to spontaneous polarisation (quantitative exemplification is given in Fig. 7).

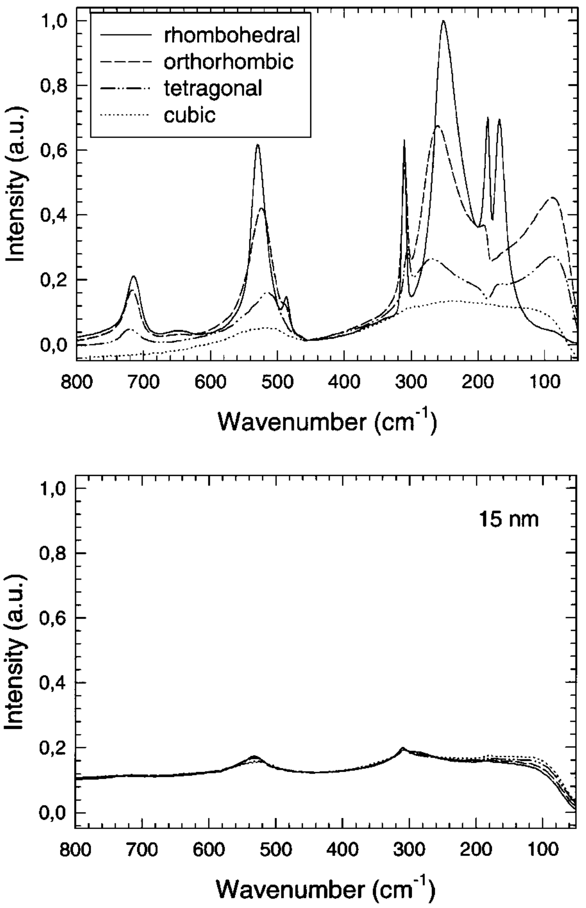

Figure 6 Size effect on temperature dependence of the Raman spectra taken from single crystal (top) and nanopowder.

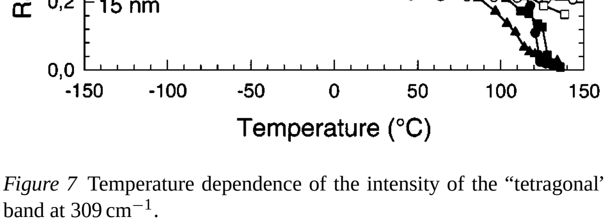

Figure 7 Temperature dependence of the intensity of the “tetragonal” band at 309 cm^{-1}.

The present paper is focussed on preparation and characterisation of ultrafine $BaTiO_3$ powders and, hence, here we confine ourselves to pointing out that the disappearance of the “tetragonal” Raman band (at 309 cm^{-1}, cf. Fig. 7), the occurrence of the “cubic” 6-line Mn^{2+} EPR spectrum (Fig. 8) and the weakening of the tetragonal quadrupole coupling interaction (Fig. 9) provide a consistent picture of the size effect on ferroelectric phase transition: The Curie point does not shift to a lower temperature (cf. [2]) but, instead, is increasingly smeared out when going to a smaller particle size. In addition, lower-symmetric tetragonal features are stabilised above Curie temperature (cf. Figs 7 and 9) while, vice versa, in small particles weak cubic admixture clearly occurs already below Curie temperature (cf. Fig. 8). The spectroscopic findings devise a

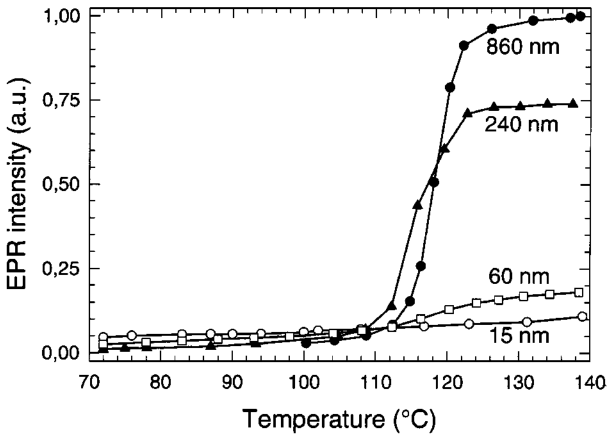

Figure 8 Size-dependent occurrence of the "cubic" Mn^{2+} 6-line EPR spectrum as observed at the ferroelectric phase transition.

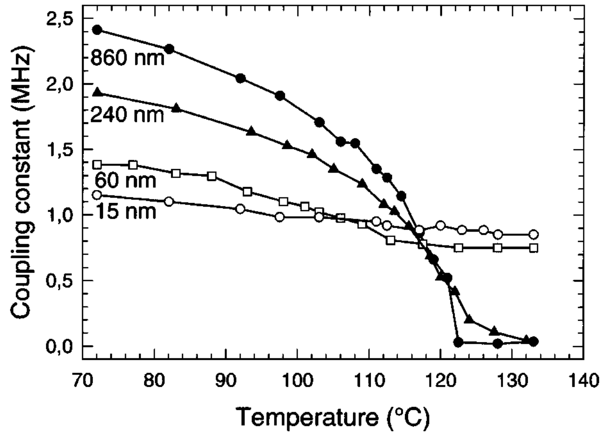

Figure 9 Temperature dependence of the nuclear quadrupole coupling constant e^2qQ/h of ^{137}Ba (I = 3/2).

picture of a small $BaTiO_3$ particle according to which a normal tetragonal core is surrounded by a tetragonally distorted surface region. A separate presentation will be given about the latter topics.

4. Conclusion

The preparation of $BaTiO_3$ ultrafine powders was achieved by polymerisation of barium titanium methacrylate as monomeric metallo-organic precursor and consecutive pyrolysis. A particularly advantageous feature of this preparation route is given by the possibility to adjust the particle size in a relatively wide size range by the tempering conditions, first of all by the reaction temperature. Doping with paramagnetic ions such as Mn^{2+}, Gd^{3+} or Cr^{3+} in a wide concentration range is readily accomplished by just adding the corresponding metal acetates to the monomeric precursors. This does not only enable EPR investigations but, moreover, allows for material modification, e.g. with respect to electric conductivity properties of PTC materials.

The concentration of lattice imperfections and impurities is obviously so low that the correlational length does not fall below geometrical dimension. This makes it possible to deduce a two-component idea of small $BaTiO_3$ particles according to which they consist of a normal tetragonal ferroelectric core which is surrounded by a tetragonally distorted outer layer. As the present route is readily applicable to the preparation of other ferroelectric perovskite-type nanopowders, an extension of the present work to studies of size-driven transition behaviour in other nano-sized perovskite-type particles is therefore hopefully envisaged.

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