



Nano-sized polymer-assisted cold sintering and recycling of ceramic composites

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Abstract

Cold sintering is an emerging technology that significantly reduces sintering temperatures by approximately an order of magnitude, down to about 100–200°C. This reduction of processing temperature enables the co-sintering and integration of dissimilar materials, such as ceramics and polymers, into unprecedented composites, where the low-energy consumption densification provides an opportunity for recycling. Here, we cold sintered barium titanate (BaTiO₃)-polytetrafluoroethylene (PTFE) ceramic-polymer composites, demonstrating that nano-sized PTFE polymer powders facilitate co-sintering and enable the recycling of ceramic composites. This approach offers an opportunity for reusing and re-processing ceramic components, thereby promoting sustainability through waste reduction and energy savings.

Introduction

With the fast development of the power electronics, dielectric materials with high permittivity, low loss, and appropriate mechanical properties are needed for many applications such as advanced pulsed capacitors and energy-storage devices.^[1] Ferroelectric ceramics, such as BaTiO₃, are promising for the aforementioned applications due to their high dielectric constant; but they typically exhibit low fracture resistance as they are prone to cracking under mechanical or thermo-mechanical loads.^[2] In contrast, polymers like polytetrafluoroethylene (PTFE) are known to be lightweight and more easily processed at lower temperatures compared to ceramics despite their poor dielectric properties.^[3] Consequently, the integration of ceramics and polymers has attracted interest in combining the desired dielectric properties of ceramic materials with the flexibility of polymers, leading to optimized electrical, mechanical and thermal properties, which makes ceramic-polymer composites highly versatile for applications in dielectrics.^[4]

Many techniques have been developed for manufacturing ceramic-polymer composites, such as tape casting, and 3D printing. Tape casting has been developed over many years, with homogenous mixture of ceramic and polymer materials processed at high temperature under vacuum.^[5] 3D printing, on the other hand, has only been recently implemented for ceramic-polymer composite fabrication. For example, processing precursors under UV light can lead to ceramic powders distributed in solidified polymers.^[6] These composites often require a polymer matrix with dispersed ceramic inclusions, which limits the amount of ceramic loading. Because limited

amounts of ceramic are scattered across the polymer matrix, the ceramic domains are rarely interconnected, which can lead to low density and poor dielectric performance.^[7]

To achieve high-density ceramics, sintering is crucial, but requires processing temperatures of around 50–75% of the melting point to activate mass transport. This facilitates reduction of the excess surface energy by driving densification and grain growth.^[8] Due to the high melting temperatures of most ceramics, it is challenging to achieve high densities of polymer-in-ceramic composites without degrading the organic component.^[7]

The high sintering temperatures required for ceramics pose another major challenge for their recycling, creating a long-standing issue in industrial waste processing.^[9] One of the most crucial factors in enabling re-processing is low-energy/temperature processing, which helps prevent side reactions that might occur at high temperatures and keeps the energy cost viable. Recycling ceramics from composites requires high sintering temperatures or excessive amounts of energy consumption, where current recycling strategies for ceramic materials through thermal processing require temperatures around 1000°C.^[10] Therefore, ceramic composites are one of the most challenging materials to reprocess, as the disparate material properties preclude existing recycling strategies.

Efforts have been made to lower the sintering temperatures of ceramics. Spark plasma sintering can produce dense ceramic products at a temperature as low as 250°C, although the technique can require complicated equipment and high cost.^[11] Hydrothermal sintering is another low-temperature method

for ceramic fabrication where a high percentage of water content is present, but the processing time can be considerably higher than conventional methods.^[12] Drawing inspiration from the natural densification processes that occurs in geological and biological mineralization, the geomimetic cold sintering process (CSP) has been developed to consolidate high-density ceramics at low temperatures (25–300°C) with the assistance of a transient liquid phase under pressure.^[7] The use of a liquid phase, typically an aqueous solution, increases the driving force for densification. The advent of cold sintering has opened up exciting opportunities to re-envision ceramic composites, particularly those with a high proportion of ceramics. The polymer can be incorporated into intergranular regions of the ceramic, dispersed throughout the ceramic matrix, or laminated between ceramic layers. The CSP also presents an attractive opportunity for composite recycling due to its low energy consumption.

For instance, BaTiO₃ is considered one of the most promising functional ceramics due to its high permittivity.^[2,13,14] As a ceramic material, the sintering temperature of BaTiO₃ is usually 1000–1500°C.^[15] In contrast, Randall et al. successfully sintered BaTiO₃ with Ba(OH)₂·8H₂O as a processing additive at a temperature as low as 225°C, and enabled co-sintering of BaTiO₃ with PTFE.^[16] Conventional ceramic-polymer composites that contain high permittivity ceramic fillers have limited amounts of ceramic loading (mostly <60 vol%), leading to relatively low permittivity (<100).^[17] The use of cold sintering led to BaTiO₃-PTFE composites with high density (approximately 95%), high permittivity, high resistivity, and enhanced mechanical properties. Nevertheless, the potential for low-temperature reprocessing and recycling of BaTiO₃ composites has not been explored.

Here, we have demonstrated that the nano-sized polymers enabled the densification and re-processing of a BaTiO₃-PTFE ceramic composite (e.g., >88–96% density) through cold sintering by integrating only 5 vol% PTFE into the grain boundaries and reforming the nanocomposite. To test the viability of composite recycling, we conducted a series of experiments, including thermal decomposition and acid washing, to repeatedly reform and re-sinter BaTiO₃-PTFE nanocomposites for multiple cycles. Recycling leads to good preservation of the dielectric properties (90%) after each cycle, without loss of densification (88–96%).

Materials and methods

BaTiO₃ nanoparticles (average particle size: 100 nm) purchased from Sigma-Aldrich were used in this research. These BaTiO₃ powders were first calcined at 800°C for 1 h to completely remove organic residues. The calcined BaTiO₃ powders were washed using 1 mol/L acetic acid aqueous solution at 80°C for 1 h to remove BaCO₃ residuals and form a thin amorphous layer,^[18] facilitating the cold sintering process. After the treatment, the powders were collected by filtration, washed with deionized water, and dried at 120°C for 24 h. Barium hydroxide octahydrate (Ba(OH)₂·8H₂O, >98%) was purchased from Alfa

Aesar. Two types of polytetrafluoroethylene (PTFE) powder were used during the experiments, with nano-fine PTFE powder (30–50 nm) obtained from Howard P. Industries and micron-level PTFE powder (1 μm) purchased from Sigma-Aldrich. These powders were used as received.

Cold sintering was carried as previously described.^[16] 0.75 g BaTiO₃ powder was mixed with 5 vol% PTFE nanoparticles using mortar and pestle with the help of ethanol. After the ethanol evaporated, 0.12 g Ba(OH)₂·8H₂O was added. To ensure we got an even-distributed mixture, after 10 min of careful mixing by hand, all the powder would go through auto-mixing. For each experiment, the mixture was loaded into a 12.7 mm diameter die and uniaxially pressed under 350 MPa. The temperature was first raised to 90°C and kept for 20 min to fully melt Ba(OH)₂·8H₂O. Then the whole system was gradually heated to 230°C and held for 90 min. Fabricated pellets were released from the die after cooling down to room temperature.

For the recycling process, the fabricated pellets from the previous cycle were turned into fine powder by grinding them down using a mortar and pestle. In order to fully remove the polymer content and excessive Ba(OH)₂, the powders were first heated at 800°C for 4 h, then washed using 1 mol/L acetic acid aqueous solution at 80°C for 1 h. After filtration, washing, and vacuum drying using a similar process as the preparation for the original powder. The collected BaTiO₃ powder was then subjected to the same cold sintering process as mentioned before. The pressure was applied before ramping up and released immediately after the dwell time. After cold sintering, the as-prepared samples were first polished with 2000 grit sandpaper, then dried under vacuum at 150°C for 24 h, and stored in the glove box to prevent water absorption.

For characterizations, bulk densities were calculated for as-sintered pellets by the geometric method. Theoretical densities were considered for pure BaTiO₃ (6.03 g/cm³) and 5 vol% PTFE-BaTiO₃ composites (5.83 g/cm³). The relative density was then calculated from the ratio between bulk densities and theoretical densities. X-ray diffraction (XRD) patterns were collected using an Empyrean (Malvern Panalytical) diffractometer operating at 45 kV and 40 mA to investigate the phase transformation between original pellets and recycled pellets. Fourier-transformed infrared spectroscopy by attenuated total reflectance (FTIR-ATR) was applied on both original and recycled composites to identify the presence of PTFE using Vertex 70 FTIR spectrometer (Bruker) under room temperature. Thermogravimetric analysis (TGA) was conducted on composites from different recycling cycles as well as the original using Discovery TGA 5500 coupled with Discovery MS (TA Instruments) in air with a heating rate of 10 °C/min. Scanning electron microscopy (SEM) images were obtained for the sintered pellets from each recycling cycle from a cross-section view at an accelerating voltage of 5 kV (Verios G4, Thermo Scientific) to investigate the microstructure changes between each cycle. Scanning electron microscopy—Energy dispersive spectroscopy (SEM-EDS) was also applied using Everhart–Thornley detector (ETD) under immersion mode to

find out the elemental distribution information among these samples. Before SEM-EDS testing, the cross-sections of cold-sintered samples were coated with 5-nm thick Ir (EM ACE600, Leica Microsystems). For dielectric property measurements, composite samples were first sputter-coated with 100-nm thick Ag on polished surfaces (Q150R Plus, Quorum Technologies) then having their capacities were measured at a frequency from 1 Hz to 1 MHz (Modulab XM MTS, Ametek Scientific).

Results and discussion

Figure 1 illustrates the process of recycling BaTiO_3 through cold sintering. PTFE is known for its high resistivity, low dielectric loss, and high alkaline stability.^[3] During the cold sintering process, the complete melting and evaporation of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ drives densification. At the same time, PTFE is homogeneously distributed in the matrix without impeding chemical reactions at the interface.^[19] The incorporation of PTFE also helps improve mechanical properties of the composites, and facilitates production of sintered samples. The final product of the BaTiO_3 -PTFE composite consists of BaTiO_3 , PTFE, and $\text{Ba}(\text{OH})_2$ resulting from the dehydration of $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. BaCO_3 may also form due to exposure to CO_2 in the air.^[20] Because PTFE can undergo thermal decomposition at temperatures between 550 and 600°C,^[21] and both

$\text{Ba}(\text{OH})_2$ and BaCO_3 can be eliminated by washing with acetic acid, we designed the recycling process based on the preparation of the BaTiO_3 powder. We increased the heating time from 1 to 4 h for the recycling process to ensure complete PTFE decomposition. The rest of the recycling process is the same as the initial preparation, including acid washing, filtration, and vacuum drying. The purified recycled BaTiO_3 powder is re-densified using cold sintering. The incorporation of PTFE enables recycling, as the polymer can be easily removed from the composite system before the next cycle begins.

We examine the effect of using different PTFE compositions on the densities and dielectric properties of the composites, as shown in Fig. 2(a). The highest dielectric constant and density are apparent for 5 vol% PTFE. The permittivity of the composites decreases as the percentage of polymer content increases, as expected from the mixing law of materials with different permittivities:^[22]

$$\varepsilon_r^n = \sum_{i=1}^N f_i \varepsilon_i^n \quad (1)$$

where ε_i is the relative permittivity, ε_r is the average composite relative permittivity, f_i is the volume fraction of the i_{th} phase, $\sum_i f_i = 1.0$, n is an exponent ranging between $-1 \leq n \leq +1$, and N is the number constituent of phases making up the composite.

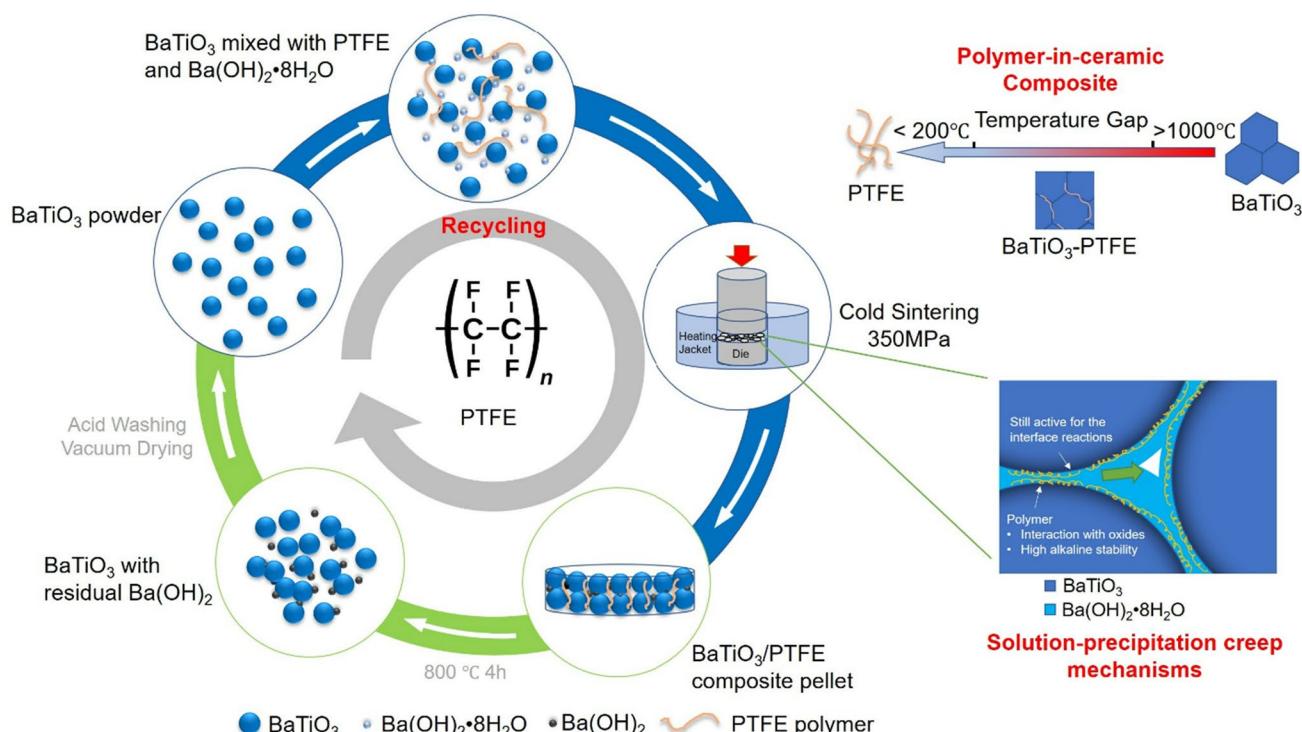


Figure 1. Schematic illustration of cold sintering and recycling process of BaTiO_3 -PTFE nanocomposites. Precipitation of dissolved ions drives densification even with adsorbed polymers at low temperature (inset). Polymers are well dispersed with oxides, allowing homogeneous distribution in the matrix without hindering chemical reactions at the interface. Such polymers can be removed through thermal decomposition, enabling recycling of BaTiO_3 .

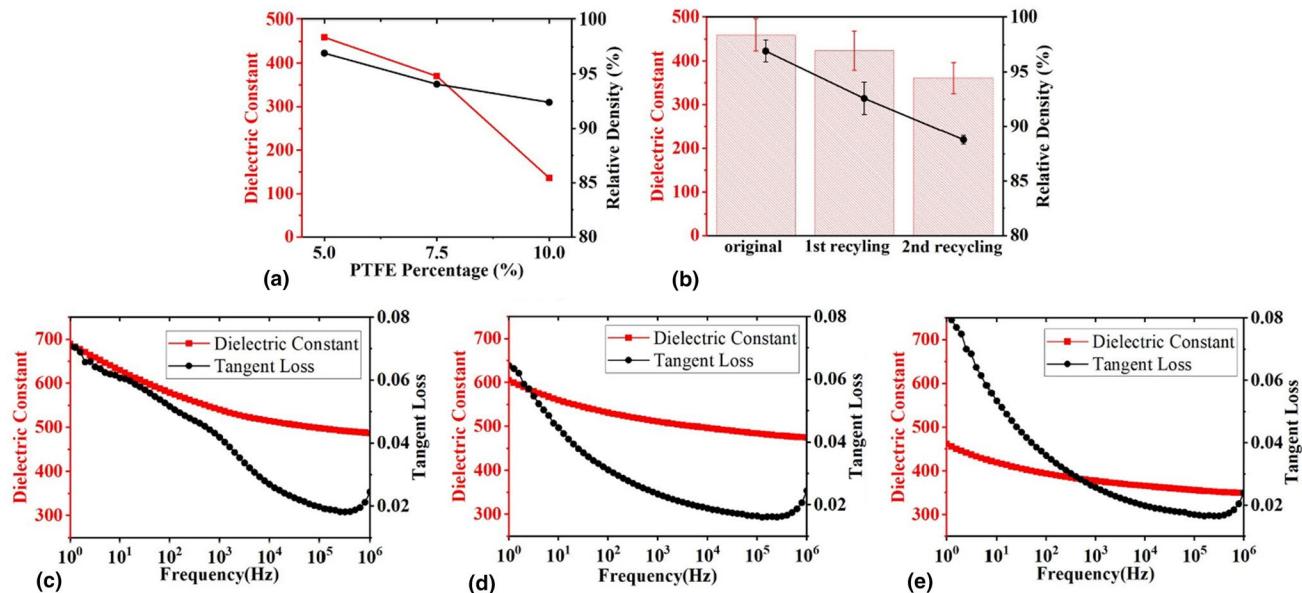


Figure 2. Comparison between dielectric constant of original and recycled BaTiO_3 -PTFE composites. (a) Dielectric constant (red squares) and density (black circles) versus polymer content. (b) Relative densities (black circles) and dielectric constant (red bars) as BaTiO_3 is recycled. Frequency dependence of dielectric constant (red squares) and tangent loss (black circles) of (c) original BaTiO_3 -PTFE composite, (d) composite after one recycling cycle, (e) composite after two recycling cycles.

We also explored the size of the PTFE particle precursors, with particle sizes of 1 micron and 50 nm, both of which were kept at a 5 vol% in the composites, as shown in Fig. S1. Overall, the polymer nanoparticles yielded higher dielectric constant (459 to 256) and higher densities (97% to 92%) compared to micron-sized polymer powders. Because the BaTiO_3 powders are around 100 nm, the use of nano-sized PTFE results in a more homogenous mixture in the final composite. Thus, we focused on 5 vol% PTFE composites with nano-sized PTFE powder precursors for reprocessing attempts.

Figure 2(b) shows a comparison of the properties of the pristine and recycled BaTiO_3 -PTFE composites. At 1 MHz, the dielectric constant of the once-recycled composite is 92.3% of the value before recycling ($\epsilon_0=459.4$, $\epsilon_1=424$). The relative density also has a modest decrease, from 96.9 to 92.6%. A second recycling attempt further decreases the dielectric constant, with only 85.1% of the original permittivity remaining ($\epsilon_1=424$, $\epsilon_2=361$). The density also continues to decrease, from 92.6 to 88.8%. The dielectric properties in the composite can be affected by various factors, such as grain size,^[23] porosity,^[24] and charge effects.^[25] We speculate that the size of BaTiO_3 powders increases with recycling, as the recycled powder is ground down directly from the composites. Consequently, when mixed with newly-added polymers, the mixture may not be as uniform as prior to recycling, which can lead to less than ideal conditions for cold sintering.^[16] Additionally, the gradual accumulation of the residuals from the thermal decomposition of polymers may also contribute to the decreasing performance of the composites as more recycling cycles are conducted. As such, we expect polymer or degraded organic

products to accumulate with each cold sintering cycle, which should lead to a decrease in permittivity.^[22] One of the potential decomposition products could be BaF_2 from reactions between PTFE and $\text{Ba}(\text{OH})_2$; the dielectric constant of BaF_2 is substantially lower than that of BaTiO_3 ($\epsilon_{\text{BaF}_2}=7.36$).^[26]

We examined the frequency-dependence of the dielectric constant, as shown in Fig. 2(c, e). The permittivity and loss tangent decrease with increasing frequency. The decrease in permittivity is attributed to the loss in space charge polarization.^[27] The accumulation of charge at grain boundaries leads to a potential barrier, resulting in higher values of the real part of the permittivity. The dielectric loss tangent is related to dielectric relaxations, or a momentary delay in the dielectric response of the material.^[28] This delay causes energy dissipation due to the polarization lagging the applied electric field due to grain boundaries. The dielectric loss of materials originates from three distinct factors: space charge migration (interfacial polarization contribution), direct current (DC) conduction, and movement of molecular dipoles (dipole loss).^[27] Our samples exhibited low energy loss, approximately 0.02 at 1 MHz. The permittivity and tangent loss versus frequency curves have similar, shallow slopes, indicating similar microstructures and grain boundary distributions across all samples irrespective of the recycling cycle.

X-ray diffraction (XRD) patterns of BaTiO_3 -PTFE composites before and after recycling are illustrated in Fig. 3(a). Peaks corresponding to BaTiO_3 reflections are apparent in all samples. In addition, BaCO_3 peaks are also observed, as highlighted in Fig. 3(b). BaCO_3 content gradually increases with each recycling cycle, possibly due to the accumulation of

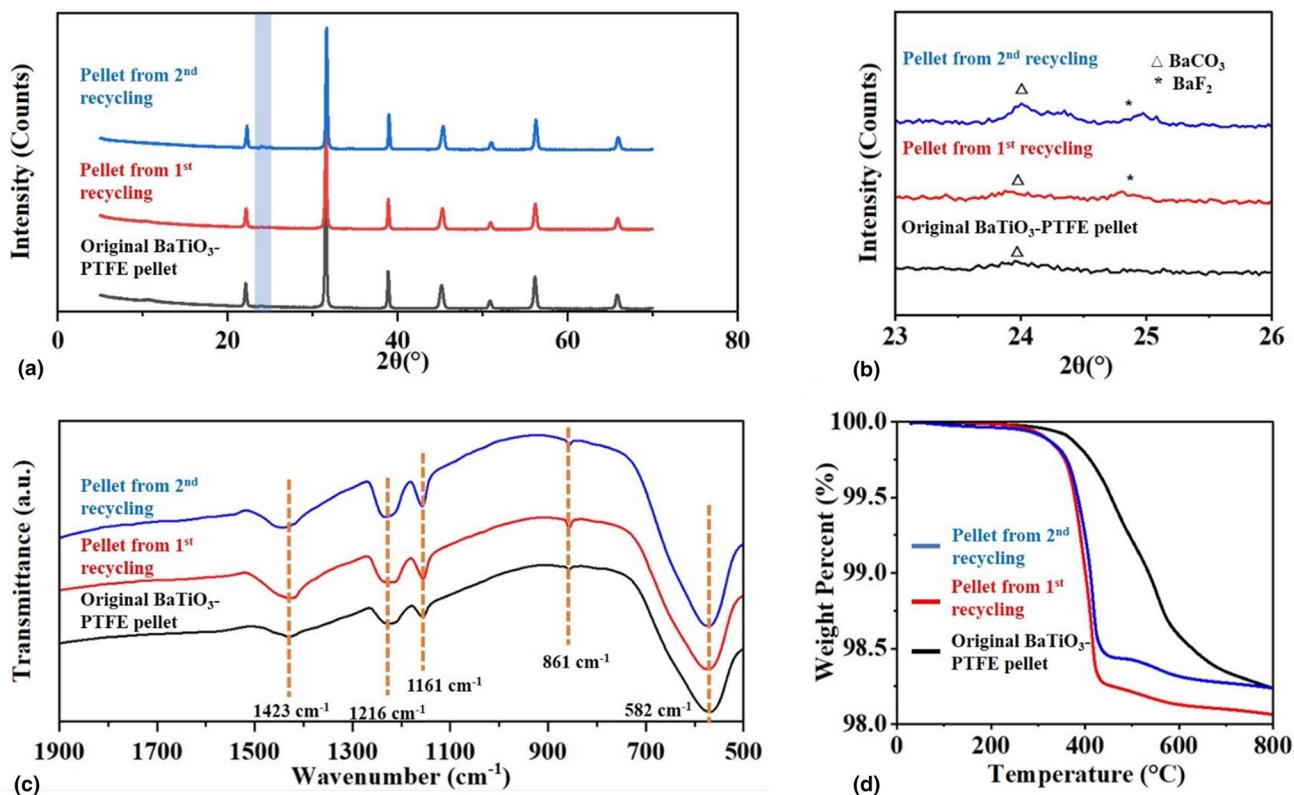


Figure 3. Characterization of pristine and recycled BaTiO₃-PTFE composites. (a, b) XRD patterns of BaTiO₃-PTFE composites from different reprocessing cycles. (c) FTIR spectra of BaTiO₃-PTFE composites before and after reprocessing. (d) TGA results of BaTiO₃-PTFE composites before and after reprocessing.

CO₂ in the system or the diminished effectiveness of the acid-washing process with recycling and re-sintering. Furthermore, the recycled composites exhibit peaks from BaF₂, which were not present in the original pellet. This supports our hypothesis that the introduction of BaF₂ negatively influences the dielectric performance, which also appears to accumulate with each re-processing cycle, likely because BaF₂ is thermally stable at high temperatures and insoluble in acetic acid.

FTIR spectra were collected for pristine and recycled composites to determine whether PTFE polymers were preserved after cold sintering and recycling processes, as shown in Fig. 3c. We observed similar characteristic bands when comparing data from pristine and recycled composites at wavenumber 1423, 1216, 1161, 861, and 582 cm⁻¹. The bands at 1423 and 861 cm⁻¹ are closely related to the out-of-plane deformation and asymmetric stretching of the nearly symmetric carbonate ion [CO₃]²⁻.^[29] The band at 582 cm⁻¹ could be from the Ti-O bond in BaTiO₃.^[20] A shift in wavenumber of cold sintered samples is apparent when compared to pure BaTiO₃ powder, which may be from particle bonding during sintering. The peaks at 1216, and 1161 cm⁻¹ are characteristic of CF₂ symmetric stretching vibrations bands,^[30] which confirms the presence of PTFE polymers after cold sintering under alkaline environments. We also observed a slight shift in these

bands, suggesting the possibility of intermolecular interactions between the surface of BaTiO₃ and PTFE polymers. Additionally, the absorption of carbonate peaks and PTFE peaks was higher in the recycled pellets than in pristine samples, indicating the accumulation of BaCO₃ impurities and PTFE polymers with increasing reprocessing. TGA also shows weight loss in samples at around 400°C, which confirms the presence of polymers in both original and recycled pellets. For 5 vol% BaTiO₃-PTFE composites, 98.3% of the mass should remain after removal of polymers, which is close to what we have left at 800°C for all samples (98.1–98.3%), indicating largely successful thermal decompositions during recycling experiments.

The SEM images of pristine and recycled BaTiO₃-PTFE cross-sections are shown in Fig. 4a–f. We observed dense and homogenous BaTiO₃ microstructures with PTFE fibers scattered across nanoparticles in pristine and recycled pellets. However, after two reprocessing cycles, polymer segregation becomes more evident, as small particles as well as large fibers filling in grain boundaries. Higher resolution SEM images provide a more detailed insight into changes at the grain boundaries as the recycling process proceeds. In the pristine sample, BaTiO₃ particles exhibit a more regular circular shape, with polymers coating the surfaces and homogeneously distributed throughout the powder. Following one reprocessing

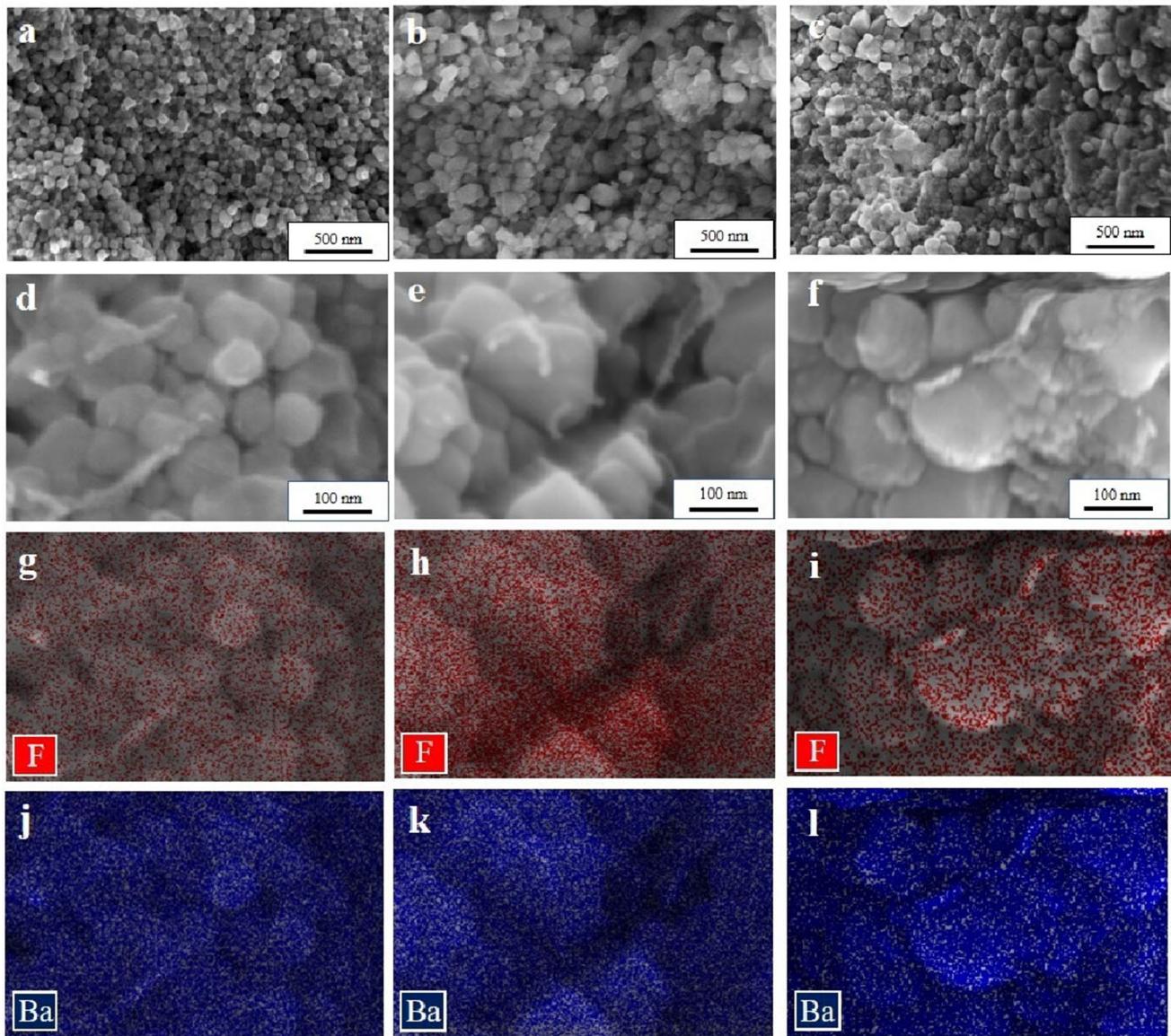


Figure 4. SEM images of original and recycled BaTiO_3 -PTFE composites. SEM images of (a, d), pristine BaTiO_3 -PTFE composite, (b, e) composite after one reprocessing cycle, (c, f) composite after two reprocessing cycles. X-ray maps of F and Ba elements of (g, j) original BaTiO_3 -PTFE composite, (h, k) composite after one reprocessing cycle, (i, l) composite after two reprocessing cycles.

cycle, BaTiO_3 particles grow in size, with the average particle size increasing from 71 to 113 nm. Although the shapes of the particles generally maintain a circular or near-circular form, irregular shapes and particle agglomeration become more evident, attributed to high-temperature calcination and excessive solution precipitation. Additionally, there is an observable increase in the level of polymer coating. Upon two reprocessing cycles, the average grain size of BaTiO_3 particles further increases from 113 to 132 nm, and polymers accumulate in the form of small particles. While the shapes of the particles are mostly preserved, the edges become noticeably rougher, with a large amount of polymer covering the particle surfaces. We

speculate that incomplete thermal decomposition after each cold sintering cycle leaves some polymer residues that accumulate over multiple cycles. Further details regarding particle size changes are provided in Table S1. The EDS analysis confirms the dominant presence of Ba with a smaller degree of F, as shown in Fig. 4(g–l). Ti, O and C are also identified as major elements across all composite samples, as shown in the X-ray maps in Fig. S2 and X-ray spectra in Fig. S3. Notably, Ir signals are detected due to Ir coating during sample preparation, and Al signals are attributed to the EDS detector itself. An increase in the amount of F in recycled samples further validates the accumulation of PTFE.

Conclusion

We have developed a closed-loop process to recycle BaTiO₃ from cold-sintered BaTiO₃-PTFE composites. Our results show that the BaTiO₃ powder can be successfully reformed via repeated cold sintering to create recycled composites while maintaining a dielectric constant that is over 90% of initial values after a single re-processing cycle. PTFE plays an essential role in facilitating co-sintering and recycling, which was confirmed by SEM images and EDS analysis of composites. During the entire sintering and recycling process, no new BaTiO₃ materials were introduced into the system, thus representing a closed-loop cold sintering process with regards to BaTiO₃. These findings provide insights into how to improve efficiency and eco-friendliness for industrial manufacturing of ceramic-polymer composites. We also highlight some directions that could continue to improve recycling of BaTiO₃ composites, including better control of the thermal decomposition of PTFE to minimize impurities (e.g., newly-formed BaF₂) and further grinding of recycled powders to enhance cold sintering and improve densification. Overall, our cold sintering approach provides cost and energy savings and enhances the potential for sustainability through recycling and re-sintering.

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Author contributions

JZ: Conceptualization, Methodology, Formal analysis, Investigation, Visualization, Writing—original draft. EDG: Conceptualization, Writing—review & editing, Supervision, Funding acquisition. HS: Conceptualization, Writing—review & editing, Supervision, Funding acquisition.

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Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Declarations

Conflict of interest

The authors declare no competing financial interests.

Supplementary Information

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