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Microemulsion mediated synthesis of $BaTiO_3$ – Ag nanocomposites

Songhak Yoon[1,*], Jürgen Dornseiffer[2], Detlev Hennings[1], Christian Pithan[1], Rainer Waser[1,3]

[1]*Insistute für Festkörperforschung (IFF), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

[2]*Instute für Chemie und Dynamik der Geosphäre (ICG), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany*

[3]*Instute für Werkstoffe der Elektrotechnik (IWE II), RWTH Aachen, Aachen, Germany*

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Abstract

$BaTiO_3$ – Ag composite nanopowders were synthesized via microemulsion mediated synthesis through the hydrolytic decomposition of mixed metal alkoxide solutions as precursor for the $BaTiO_3$ and the reduction of silver nitrate in the presence of polyvinylpyrrolidone (PVP) as source for the Ag nanoparticles. The X-ray diffraction (XRD) patterns indicate that $BaTiO_3$ and Ag phases were successfully synthesized in the composite powders. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) show that the synthesized $BaTiO_3$ nanoparticles were aggregates of nanosized primary particles as small as 10 nm in diameter and the average particle size of nanocrystalline Ag was about 100 nm. Calcination and sintering studies reveal that there exists a difference in the sintering behaviour of $BaTiO_3$ and Ag in the composite nanopowders. Thermogravimetric analysis (TGA) shows weight losses due to the burnout of organic residues arising from the synthesis, the release of water from the surface and separation of hydroxyl ions from the lattice of $BaTiO_3$ nanoparticles. A dilatometric study of $BaTiO_3$-Ag composite confirmed a strong difference in the shrinkage behaviour compared to that of the pure $BaTiO_3$ obtained by microemulsion mediated synthesis.

Keywords: *nanoparticulate synthesis, ceramic processing, $BaTiO_3$-Ag nanocomposites, cermets*

I. Introduction

Ceramic-metal nanocomposite materials are extensively used in many technological applications due to enhanced mechanical, optical, electrical or magnetic properties, which are not achievable for monolithic materials [1–3]. It makes them excellent candidates for the fabrication of multifunctional devices with unique features and much effort has been undertaken to design and control their microstructure for new applications. Several processes have been developed for the preparation of nanoscale ceramic-metal composite powders to be sintered into consolidated nano-cermets. These processes include mechanical milling [4], reactive metal penetration [5], electrochemical infiltration [6], the combustion method [7], self-propagating high-temperature synthesis (SHS) [8], the sol–gel method [9], and the heterogeneous precipitation method [10]. Although each technique has its own advantages, most of them have been found to be inadequate to produce composite nanopowders with an average particle size smaller than 100 nm.

With respect to this, colloidal approaches such as microemulsion mediated synthesis are believed to have a high potential for the realization of tailor-made nanocomposites because the particle size and size distribution can be controlled easily on the nanoscale and mixing of all constituents, ceramic and metallic phases, can be carried out very homogeneously. In recent years, several technologically important ceramic systems have been synthesized from water-in-oil microemulsions [11–13]. Microemulsions are liquid, transparent, optically isotropic and thermodynamically stable dispersions of a polar and a non-polar solvent, typically water or an aqueous solution and a liquid hydrocarbon. Droplets of only 1–100 nm in size are stabilized by the addition of surfactants and thus particle sizes down to a few tens of nanometers or even only several nanometers can be achieved by restricting crystal growth during particle formation. Herrig and Hempelmann [14] reported that microemulsion-derived ceramic powders of

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[*] Corresponding author: tel: +49 2461 61 5016
fax: +49 2461 61 2550 , e-mail: *s.yoon@fz-juelich.de*

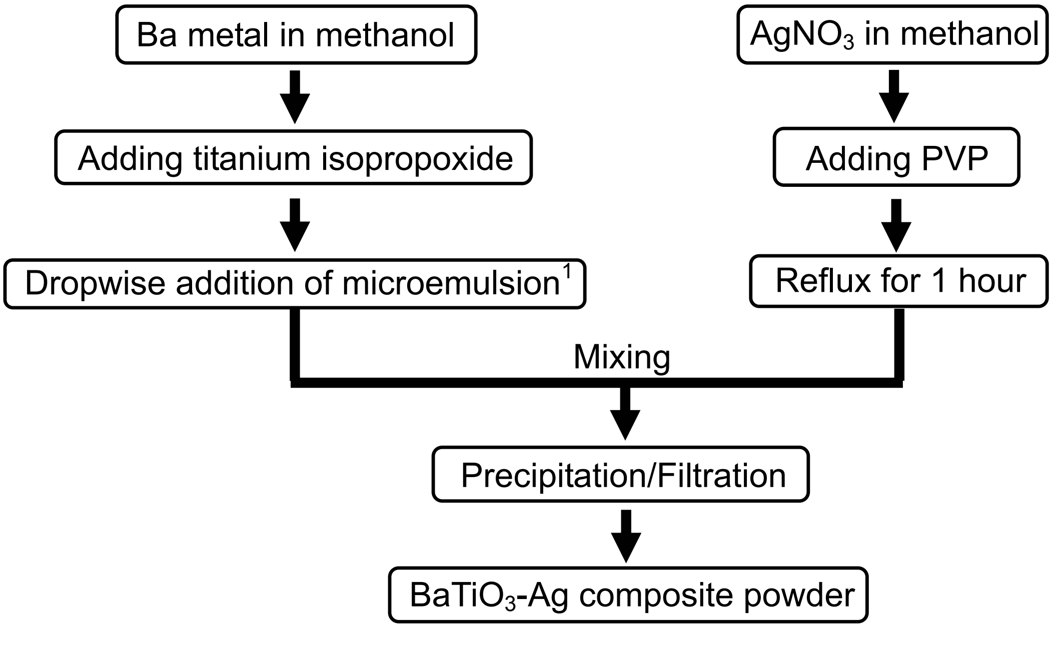
$BaTiO_3$ are much finer in particle size, narrower in particle size distribution and higher in both composition homogeneity and sinterability than those prepared via many other chemical synthesis routes. However, there are only very few reports on the preparation of $BaTiO_3$-metal composite nanoparticles by microemulsion until now.

$BaTiO_3$ and its related compounds are widely used as thermistors, capacitors, gate dielectrics, memories, and power-storage devices in recent years [15–17]. Materials with high dielectric constant are crucial to satisfy the current trend of miniaturization and improved performance in electronic devices and $BaTiO_3$-Ag composites has attracted much attention due to the strongly enhanced dielectric constant [18].

In this study, $BaTiO_3$-Ag composite nanopowders were synthesized via microemulsion mediated synthesis. This modified synthetic route has been developed in order to prepare homogeneously dispersed composite nanoparticles of metal and ceramic. The microstructure evolution and sintering behaviour are investigated.

II. Experimental

$BaTiO_3$-Ag composite nanopowders with 20 wt.% of silver were synthesized by mixing a silver nanoparticle dispersion with a barium titanate nanoparticle dispersion. The synthetic procedures for the preparation of the colloidal $BaTiO_3$ suspension were performed using the Schlenk technique under argon. CO_2 contamination of the argon gas was minimized using a CO_2-adsorber column for gas purification. 2.355 g of pure Ba metal (> 99% metal basis, Alfa Aesar GmbH & Co., KG, Karlsruhe, Germany) was dissolved in 150 ml of methanol which was dried over a molecular sieve (0.3 nm, beads, Merck Eurolab GmbH). 4.875 g of titanium isopropoxide (synthetic grade, Merck Eurolab GmbH, Germany) was added to the previously prepared barium methanolate solution. All starting chemicals used for precursor preparation were stored in gastight glass vessels in an Ar-glove box. After the preparation of the precursor solutions, 8.253 g of a microemulsion was added dropwise through a dropping funnel into the reaction vessel in order to form the nano-sized $BaTiO_3$ particles. The microemulsion contained 3.74 wt.% of CTAB (cetyl trimethylammonium bromide, Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany), 72.82 wt.% of cyclohexane (analytical grade, Riedel de Haën, Seelze, Germany), 12.21 wt.% of 1-pentanol (analytical grade, Merck, Eurolab GmbH, Germany), and 11.23 wt.% of degassed water. For the preparation of the Ag-dispersion, 1.574 g of silver nitrate (Merck, Darmstadt, Germany) was dissolved in 150 ml methanol (Merck, Darmstadt, Germany) in the presence of 2.4 g polyvinylpyrrolidone (PVP, average molar weight M = 10000 g/mol, Fluka, Steinheim, Germany) and heated under reflux for 1 hour. Subsequently, the obtained dark red solution which contained the silver nanoparticles was mixed with the methanolic solution of the $BaTiO_3$ na-



[1] The microemulsion contained CTAB (cetyl trimethylammonium bromide) (3.74 wt.%), cyclohexane (72.82 wt.%), 1-pentanol (12.21 wt.%) and water (11.23 wt.%)

Figure 1. Flow chart for the synthesis of $BaTiO_3$-Ag composite nanopowders using microemulsion-mediated synthesis

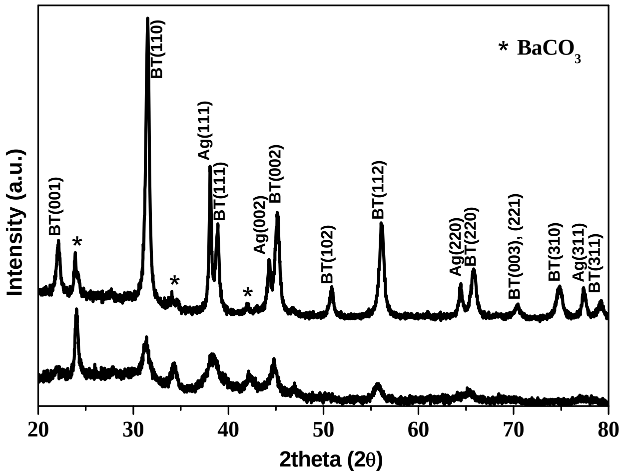


Figure 2. XRD patterns of the as-synthesized $BaTiO_3$-Ag composite powder and that of calcined one (600°C for 1h)

noparticles. After mixing both solutions, the powder was isolated, purified using Soxhlet extraction with cyclohexane and finally dried in vacuum. Fig. 1 presents the flow chart of the microemulsion mediated method developed for the synthesis of $BaTiO_3$-Ag composite nanopowders.

With the synthesized powders, phase identification was performed by powder X-ray diffraction (XRD, Philips X'PERT, Koninklijke Philips Electronics N.V., Eindhoven, the Netherlands). The incident X-rays had a wavelength of 1.5418 Å due to combined application of Cu $K_{\alpha 1}$ and Cu $K_{\alpha 2}$ radiation. The diffraction pattern was scanned from 20° to 80° (2θ) with a step size of 0.01°. The particle size and homogeneity of $BaTiO_3$ and Ag distribution of the synthesized composite nanopowders were characterized by field emission scanning electron microscopy (FE-SEM, LEO1530, Carl Zeiss AG, Jena, Germany) operating at 20 kV in combination with energy dispersive X-ray analysis (EDX) and transmission electron microscopy (TEM, CM-200, Koninklijke Philips Electronics N.V., Amsterdam, the Netherlands) operating at 200 kV. The samples for TEM were prepared by dropping the solution mixture of $BaTiO_3$ and Ag on a carbon coated Cu-grid and drying in air. Thermogravimetric analysis of the initial powders (TGA, STA 429, Netzsch Gerätebau GmbH, Selb, Germany) was carried out under Ar-atmosphere in the temperature range from 25°C to 900°C with heating and cooling rates of 20 K/min, respectively. The sintering behaviour of the raw powder was investigated using dilatometry (DIL 402 C, Netzsch Gerätebau GmbH, Germany) under Ar atmosphere in the temperature range from 25°C to 1000°C also with heating and cooling rates of 20 K/min, respectively. For this purpose a cylindrical sample with a diameter 10 mm was compacted by uniaxial pressing applying a force of 63.7 MPa followed by cold isostatic press at 815 MPa. The green density of the powder pellet was 3.844 g/cm^3 (55.4% of the theoretic density). The surface morphology and microstructure of the sintered samples after the dilatometric measurement were studied using optical microscopy (OM, Axioplan 2, Carl Zeiss MicroImaging GmbH, Jena, Germany) and scanning electron microscopy (SEM, model S-4100, Hitachi, Tokyo, Japan).

III. Results and discussion

The X-ray diffraction (XRD) patterns of the as-synthesized $BaTiO_3$-Ag composite powders with 20 wt.% of silver and that of calcined powders at 600°C for 1hr are shown in Fig. 2. Observed Bragg diffraction peaks were identified to belong either to $BaTiO_3$ (JCPDS 31-0174) or Ag (JCPDS 03-0921) and $BaCO_3$ appears as indicated in the spectra. However, we found no evidence of carbonate formation as the reaction was performed [19]. This indicates that the carbonate formation is due to aging at air during sample storage. After annealing at 600°C for 1hr, the diffraction peak of $BaTiO_3$ and Ag increased in intensity and sharpened relatively to those measured for the raw product due to crystal growth. The XRD diffraction patterns indicate that no other major phases than $BaTiO_3$ and Ag were present in the composite powders.

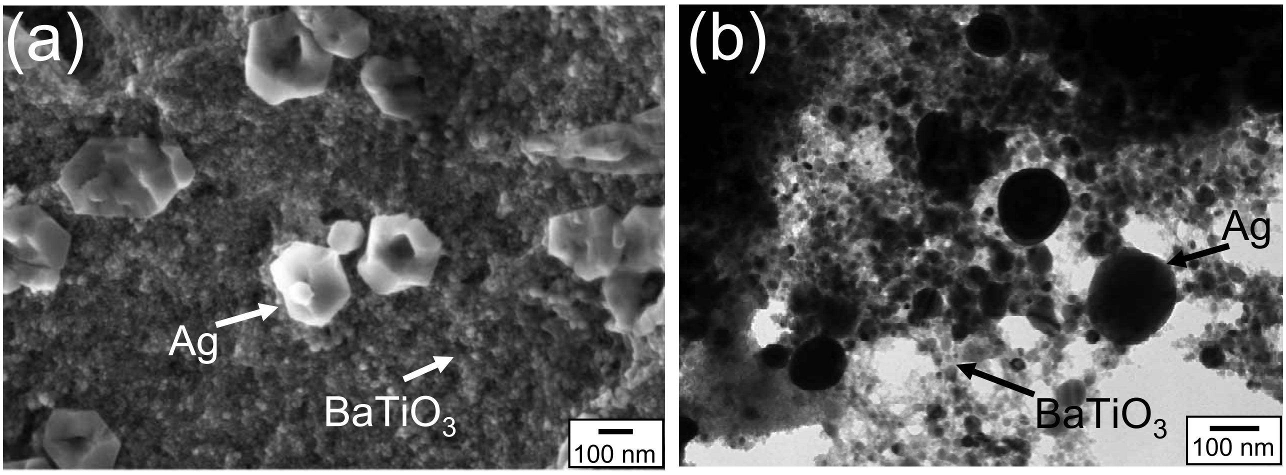


Figure 3. SEM (a) and TEM (b) pictures of as-synthesized $BaTiO_3$ and silver nanoparticles

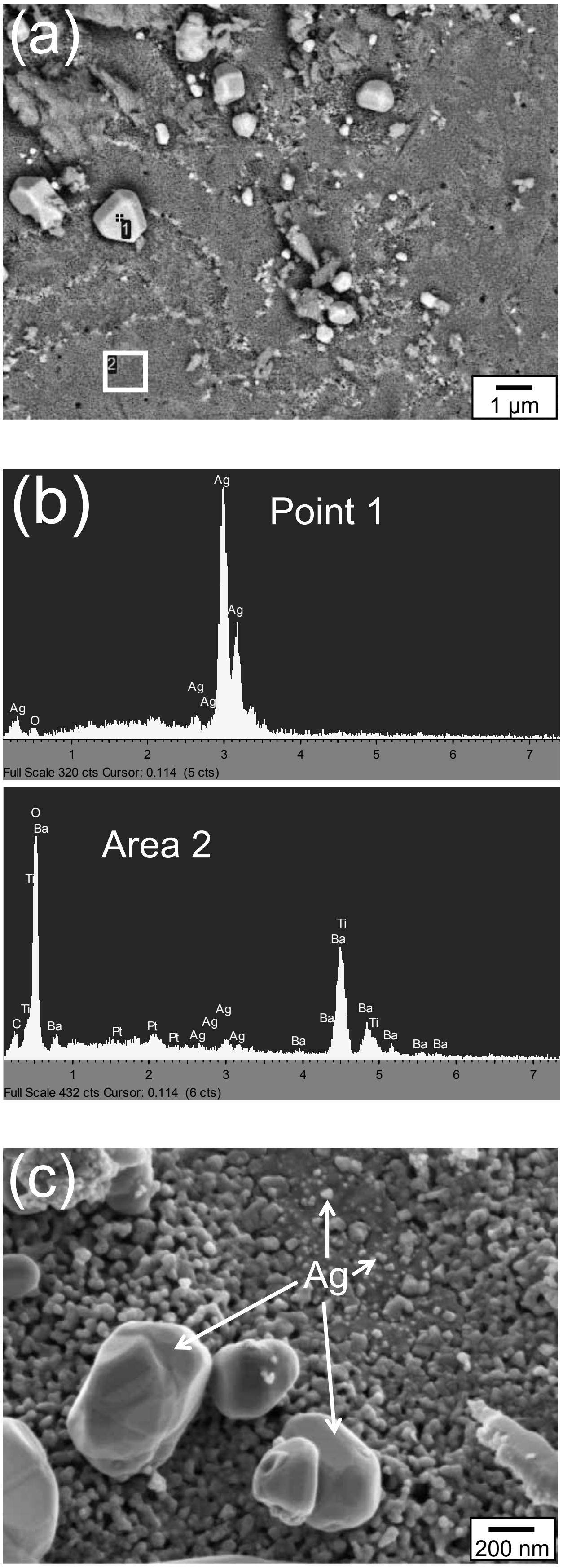


Figure 4. SEM picture (backscattered electron image) of powders calcined at 600°C for 1h (a), EDX spectra of Point 1 and Area 2 (b) and enlarged SEM photograph (secondary electron image) (c).

Fig. 3 shows SEM and TEM pictures of the as-synthesized $BaTiO_3$ and silver nanoparticles. The average silver particle size was estimated to be about 100 nm and that of $BaTiO_3$ was less than 10 nm [19]. Fig. 3b clearly shows that $BaTiO_3$ particles are formed by the aggregation of nanometer-sized fine particles, smaller than 10 nm in diameter.

The phase morphology of $BaTiO_3$-Ag composite powders calcined at 600°C for 1hr is shown in Fig. 4a. The results of EDX analysis shown in Fig. 4b indicate that the micron-size bright particles which are seen in Fig. 4a consist of pure silver, possibly slightly oxidized, with no trace of Ba, Ti, O. The EDX analysis of the matrix area marked in Fig. 4a gave evidence for the presence of Ba, Ti, O and traces of Ag, which implies that ultrafine Ag nanoparticles are also distributed in the $BaTiO_3$ matrix. Fig. 4c, an enlarged SEM photograph, clearly shows that ultrafine Ag nanoparticles as well as larger Ag particles are distributed in the $BaTiO_3$ matrix.

Fig. 5 shows the TGA curve of the as-prepared $BaTiO_3$-Ag composite nanopowders. The results of these measurements reveal several steps of mass losses. The first weight loss amounts to 21.91 % occurs up to a temperature of approximately 450°C and is attributed to the burnout of residual organics arising from the synthesis (e.g. surfactant) from the composite powders and the release of physisorbed water on the surface of $BaTiO_3$ nanopowders [20,21]. The second weight loss of 9.81 % occurs in a wide range of temperatures up to 900°C and mainly results from the release of chemisorbed water and/or incorporated hydroxyl ions in the lattice of $BaTiO_3$. Thus, it is apparent that the as-prepared $BaTiO_3$-Ag nanopowders possess high concentration of organics, water, and hydroxyl ions.

In order to study the sinterability of the synthesized composite nanoparticles a dilatometric analysis was

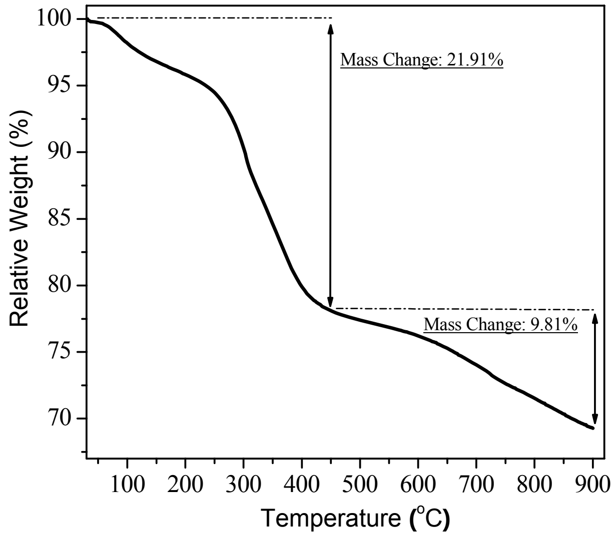


Figure 5. TGA traces measured with a heating rate of 20 K/min in Ar atmosphere from 25°C up to 900°C for the as-prepared $BaTiO_3$-Ag composite nanopowders

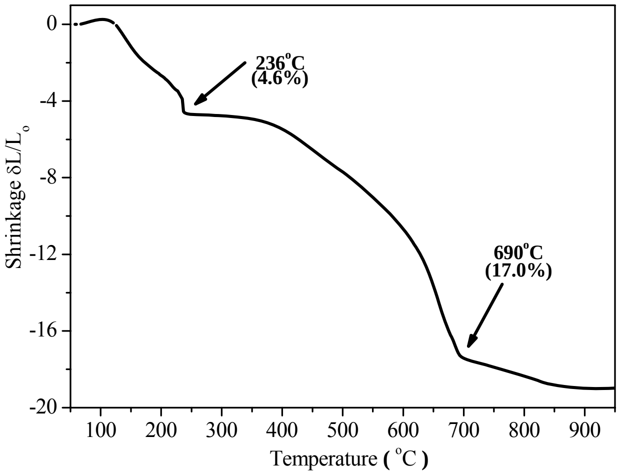


Figure 6. Dilatometry curve of $BaTiO_3$-Ag composite powder at a heating rate of 20 K/min in Ar atmosphere

carried out. The linear shrinkage curve of the sample is presented in Fig. 6. With the introduction of Ag nanoparticles into the $BaTiO_3$, the dilatometric shrinkage observed up to approximately 700°C is about 17.0 % which is much higher compared to that of pure $BaTiO_3$ obtained by microemulsion mediated synthesis (linear shrinkage about 5.0 %) [19]. The coalescence of Ag is probably related to the enhanced sinterability of composite compared to the pure $BaTiO_3$.

Fig. 7a shows the polished surface of a $BaTiO_3$-Ag composite sintered at 700°C for 1h. As observed by optical microscopy, it shows that silver particles (bright) agglomerate during sintering and form filaments. In an enlarged SEM photograph (Fig. 7b), no evidence of substantial grain growth for the ultrafine $BaTiO_3$ nanoparticles can be observed. Silver nanoparticles, however, form micron-size particles upon sintering and grain growth. These results reflect a different sintering behaviour for $BaTiO_3$ and Ag nanoparticles.

With the addition of silver, previous reports showed that ceramic-Ag composite can be sintered at much lower temperatures with enhanced sinterability compared to the pure ceramic phase [22–24]. Hwang *et al.* for example showed that the densification of PZT was accelerated by the addition of silver particles without the formation of filaments [24]. Panteny *et al.*, on the other hand, founded that silver addition reduced the final sintered density in $BaTiO_3$-Ag composites [25]. In our study, the synthesized silver nanoparticles are 100 nm or less in size and consequently they start to sinter at much lower temperatures around 125°C. Moon *et al.*, also presented that coalescence of the Ag nanoparticles (about 20 nm) starts at significantly lower temperature (~ 150°C) compared to that of the bulk material [26]. Additionally, filament formation was observed, for the reasons not yet understood. Further investigations are needed in order to obtain a clear picture of the sintering behaviour of $BaTiO_3$-Ag composites synthesized by microemulsion mediated synthesis.

IV. Conclusions

$BaTiO_3$-Ag nanocomposite powders were successfully prepared via microemulsion-mediated synthesis. The synthesized $BaTiO_3$ nanoparticles were aggregates of nanosized primary particles as small as 10 nm and the size of Ag nanoparticles was about 100 nm. Calcined and sintered $BaTiO_3$-Ag composite powders reveal a different sintering behaviour of $BaTiO_3$ compared to Ag nanoparticles in composite nanopowders. More specifically the ultrafine Ag nanoparticles start to form elongated filaments at 700°C due to the coarsening process. It is anticipated that modified microemul-

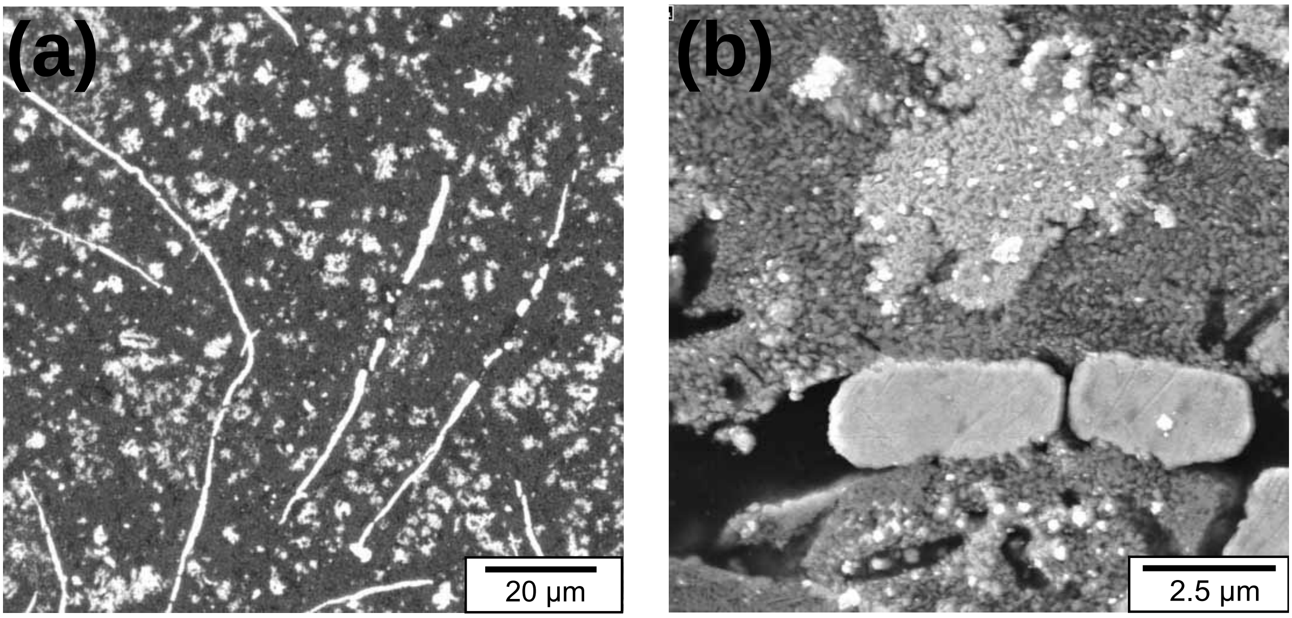


Figure 7. Optical micrograph (a) and scanning electron micrograph (b) of the polished surface of $BaTiO_3$-Ag composite sintered at 700°C for 1h

sion synthetic route can be adapted for the preparation of the novel $BaTiO_3$-metal nanocomposite powders for new concepts in ceramic materials and their potential applications.

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References

1. S. Komarneni, "Nanocomposites", *J. Mater. Chem.,* **2** [12] (1992) 1219–1230.
2. H. Kondo, T. Sekino, N. Tanaka, T. Nakayama, T. Kusunose, K. Niihara, "Mechanical and magnetic properties of novel yttria-stabilized tetragonal zirconia/Ni nanocomposite prepared by the modified internal reduction method", *J. Am. Ceram. Soc.*, **88** [6] (2005) 1468–1473.
3. C. Pecharromán, F. Esteban-Betegón, J.F. Bartolomé, S. López-Esteban, J.S. Moya, "New percolative $BaTiO_3$-Ni composites with a high and frequency-independent dielectric constant ($\varepsilon_r \approx 80\,000$)", *Adv. Mater.*, **13** [20] (2001) 1541–1544.
4. L.X. Qiu, B. Yao, Z.H. Ding, Y.J. Zheng, X.P. Jia, W.T. Zheng, "Characterization of structure and properties of TiN–TiB_2 nano-composite prepared by ball milling and high pressure heat treatment", *J. Alloys Compd.*, **456** [1-2] (2008) 436–440.
5. X.M. Xi, X.F. Yang, "Spontaneous infiltration of aluminum-silicon alloy into silicon carbide preforms in air", *J. Am. Ceram. Soc.*, **79** [1] (1996) 102–108.
6. T.J. Lee, K.G. Sheppard, Y.Q., Li, B. Gallois, "Synthesis of a nanophase, whisker-reinforced, ceramic/metal composite by electrochemical infiltration", *J. Mater. Sci.*, **31** [24] (1996) 6555–6563.
7. B. Moreno, E. Chinarro, J.L.G. Fierro, J.R. Jurado, "Synthesis of the ceramic-metal catalysts (PtRuNi-TiO_2) by the combustion method", *J. Power Sources*, **169** [1] (2007) 98–102.
8. H.E. Camurlu, "Synthesis of zirconium diboride-zirconium nitride composite powders by self-propagating high-temperature synthesis", *J. Mater. Sci.*, **42** [24] (2007) 10288–10295.
9. J.P. Wang, H.L. Luo, "Preparation and properties of pure nanocomposite Fe-SiO_2 using thesol-gel method", *J. Magn. Magn. Mater.*, **131** [1-2] (1994) 54–60.
10. J.X. Zhang, L.Q. Gao, "Nanocomposite powders from coating with heterogeneous nucleation processing", *Ceram. Int.*, **27** [2] (2001) 143–147.
11. J. Fang, J. Wang, S.-C. Ng, C.-H. Chew, L.-M. Gan, "Ultrafine zirconia powders via microemulsion processing route", *Nanostruct. Mater.*, **8** [4] (1997) 499–505.
12. J. Wang, J. Fang, S.-C. Ng, L.-M. Gan, Ch.-H. Chew, X. Wang, Z. Shen, "Ultrafine barium titanate powders via microemulsion processing routes", *J. Am. Ceram. Soc.*, **82** [4] (1999) 873–881.
13. C. Beck, W. Härtl, R. Hempelmann, "Size-controlled synthesis of nanocrystalline $BaTiO_3$ by a sol-gel type hydrolysis in microemulsion-provided nanoreactors", *J. Mater. Res.*, **13** [11] (1998) 3174–3180.
14. H. Herrig, R. Hempelmann, "A colloidal approach to nanometre-sized mixed oxide ceramic powders", *Mater. Lett.*, **27** [6] (1996) 287–292.
15. A.J. Moulson, J.M. Herbert, *Electroceramics: Materials, Properties, Applications*, John Wiley & Sons Ltd., West Sussex, U.K. 2003.
16. P.P. Phule, S.H. Risbud, "Low-temperature synthesis and processing of electric materials in the BaO–TiO_2 System", *J. Mater. Sci.*, **25** (1990) 1169–1183.
17. D. Hennings, M. Klee, R. Waser, "Advanced dielectrics: bulk ceramics and thin films", *Adv. Mater.*, **3** [7-8] (1991) 334–340.
18. S. Panteny, C.R. Bowen, R. Stevens, "Characterisation of barium titanate-silver composites part II: electrical properties", *J. Mater. Sci.,* **41** [12] (2006) 3845–3851.
19. C. Pithan, Y. Shiratori, R. Waser, J. Dornseiffer, F.-H. Haegel, "Preparation, processing, and characterization of nano-crystalline $BaTiO_3$ powders and ceramics derived from microemulsion-mediated synthesis", *J. Am. Ceram. Soc.,* **89** [9] (2006) 2908–2916.
20. J. Qi, L. Li, Y. Wang, Z. Gui, "Preparation of nanoscaled $BaTiO_3$ powders by DSS method near room temperature under normal pressure", *J. Cryst. Growth*, **260** [3-4] (2004) 551–556.
21. V. Kumar, "Solution-precipitation of fine powders of barium titanate and strontium titanate," *J. Am. Ceram. Soc.*, **82** [10] (1999) 2580–2584.
22. S. George, J. James, M.Th. Sebastian, "Giant permittivity of a bismuth zinc niobate-silver composite", *J. Am. Ceram. Soc.*, **90** [11] (2007) 3522–3528.
23. Y. Lin, C-W. Nan, J. Wang, G. Liu, J. Wu, N. Cai, "Dielectric behavior of $Na_{0.5}Bi_{0.5}TiO_3$-based composites incorporating silver particles", *J. Am. Ceram. Soc.*, **87** [4] (2004) 742–745.
24. H.J. Hwang, K. Watari, M. Sando, M. Toriyama, K. Niihara, "Low-temperature sinteirng and high-strenth $Pb(Zr,Ti)O_3$-matrix composites incorporating silver particles", *J. Am. Ceram. Soc.*, **80** [3] (1997) 791–793.
25. S. Panteny, C.R. Bowen, R. Stevens, "Characterisation of barium titanate-silver composites, part I: microstructure and mechanical properties", *J. Mater. Sci.*, **41** [12] (2006) 3837–3843.
26. K-S. Moon, H. Dong, R. Maric, S. Pothukuchi, A. Hunt, Y. Li, C.P. Wong, "Thermal behavior of silver nanoparticles for low-temperature interconnect applications", *J. Electronic Mater.*, **34** [2] (2005) 168–175.