Journal of the European Ceramic Society 21 (2001) 1689–1692

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Mechanochemical synthesis of $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ dielectric ceramics

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Received 4 September 2000; received in revised form 5 December 2000; accepted 10 December 2000

Abstract

In the last years, mechanochemical alloying has been proven to be an important technology for the synthesis of intermetallic compounds. This technology has recently been used as a new route for the synthesis of inorganic compounds. The use of mechanochemical synthesis opens possibilities for the synthesis of complex systems at low temperatures. In this paper we discuss the preparation of the powders $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ by mechanochemical synthesis. Phase formation is studied by X-ray powder diffraction. Since partly amorphous powders are obtained the crystallisation behaviour is further investigated by high temperature X-ray powder diffraction. Ceramic pellets have been sintered starting from as-milled powders as well as prefired powders. Microstructure and dielectric properties are characterised.

Keywords: $BaTiO_3$ and titanates; Dielectric properties; Mechanochemical synthesis; Niobates

1. Introduction

Mechanochemical synthesis has been proven to be a preparation technique, which allows the formation of various materials. In the last years an increasing interest in mechanochemical syntheses of dielectric materials is reported.[1–5] In these reports the information about dielectric properties and contamination degree of the formed materials is limited.[4,5] In this work we present results on mechanochemically synthesised $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$. $BaTiO_3$ has been chosen as a reference material because this material is well studied. $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ are materials of increasing interest as lead free piezo-ceramics.

2. Experimental procedure

Commercially available BaO_2 (zur Analyse, purity >99%, Merck), TiO_2 (purity >98%, ACROS), Nb_2O_5 (purity >99%, H.C. Starck), Na_2O_2 (zur Analyse, purity >95%, Merck) and Bi_2O_3 (purity >98%, Fluka) were used as starting materials in this work. To prepare the compounds $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ the appropriate amounts of the oxides were mechanochemically milled. Ten stainless steel balls of diameter 25 mm were used in a vertical ball mill UBM-II (Australian Scientific Instruments) which was operated at 100 rpm. It is possible to mill at room temperature up to 200°C. The gas-tight chamber is suitable for both milling under vacuum as well as conditioned atmosphere up to 700 kPa. The UBM-II is not suitable to prepare large quantities of materials within a short time. Due to the prolonged milling time, the reaction can be monitored by analysing intermediate samplings. Each batch contained 30 g of powder. Our milling experiments were carried out at 25°C in nitrogen atmosphere. At time intervals samples were taken and examined by X-ray diffraction, XRD (Philips, PW-1800), transmission electron microscopy, TEM (Philips, EM400), scanning electron microscopy, SEM (Philips, SEM XL40) and electron probe microscopy analyses, EPMA (Philips, microspec WDX 600). The contamination of the powders, due to the milling process, was determined by wet chemical analyses.

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00095-4

Before pressing pellets, the milled powders have been granulated. Uni-axial pressed pellets (diameter 6 mm, thickness 0.5 mm) have been sintered in air at 1100–1350°C (heating rate 300°C/h — 1 h at top — cooling 300°C/h). The density of sintered ceramics has been determined by Archimedes' method. The dielectric constant has been measured on pellets with a diameter of approx. 5 mm and a thickness of about 0.4 mm with Ni/Cr+Au contacts. The measurement was performed at 10 kHz at 1 V between −50 and 150°C using an S&A sample chamber (S&A Inc., Scottsdale Arizona, 2255 controller) and a HP4284A LCR meter.

3. Results and discussion

3.1. $BaTiO_3$

As shown in Fig. 1 after 0.5 h milling the starting materials BaO_2 and TiO_2 are still present. Also some $BaCO_3$ is detected which is present as contamination in the starting material BaO_2. After prolonged milling line broadening of diffraction peaks of BaO_2 and TiO_2 was observed and formation of $BaTiO_3$ was noticed. Almost single phase $BaTiO_3$, with a trace of TiO_2, was obtained after 256 h of milling.

To examine the reaction during mechanochemical syntheses also SEM (on powders) and EPMA analyses (on cross-sections of pressed pellets) were carried out at different time intervals of milling. Still after 0.5 h of milling (Fig. 2a) the large particles of BaO_2 and the small particles of TiO_2 are clearly present. After 8 h of milling an intense mixing of the oxides was obtained (Fig. 2b). According to XRD the major phases present were BaO_2 and TiO_2. After 128 h of milling the morphology of the particles (Fig. 2c) did not change much but XRD revealed as major phase $BaTiO_3$.

With EPMA the distribution of the elements Ba and Ti are shown after 0.5, 8 and 128 of milling (Fig. 3).

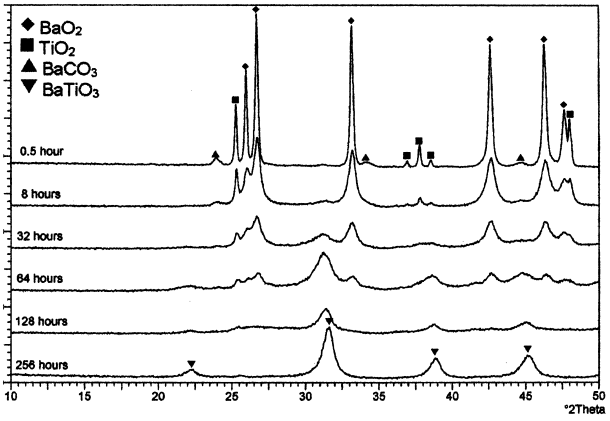

Fig. 1. XRD pattern of milled $BaTiO_3$ composition at various time intervals.

After 0.5 h of milling (Fig. 3a and b) still large areas of BaO_2 are clearly observed. The homogeneity of Ba and Ti after 8 h (Fig. 3c and d) of milling is not improved much after 128 h (Fig. 3e and f) of milling.

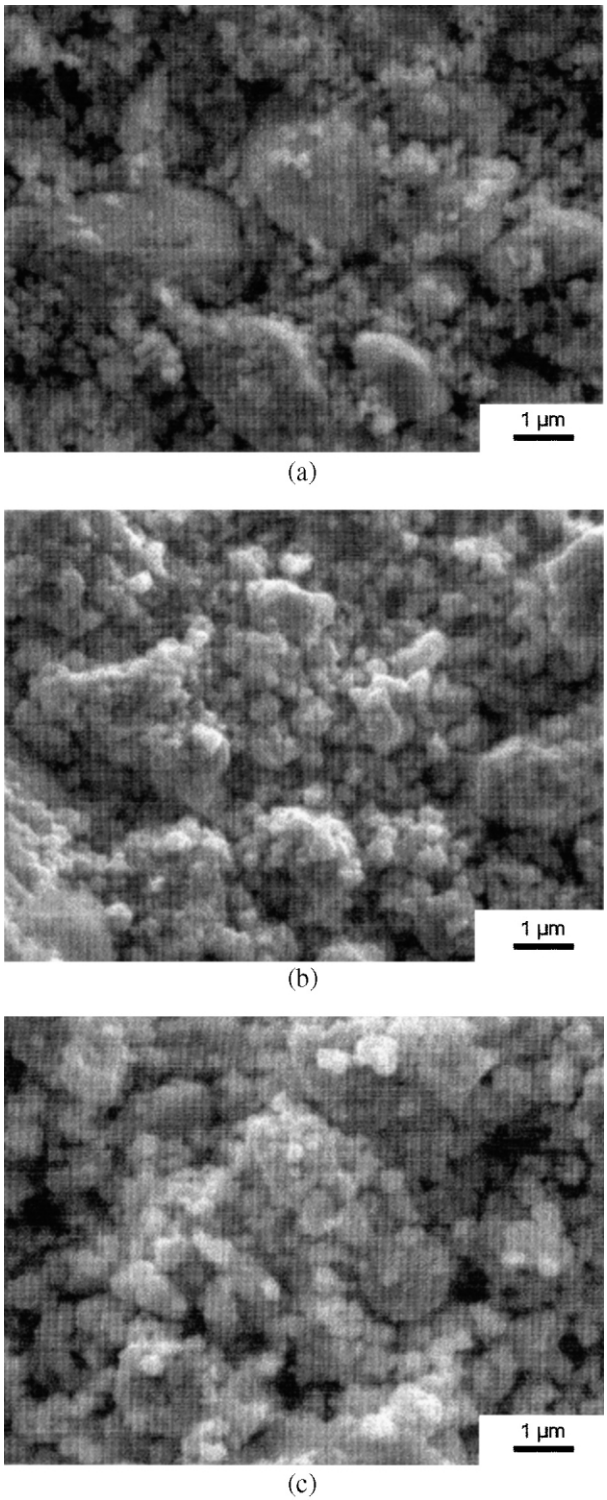

Fig. 2. SEM micrographs of $BaTiO_3$ powders after (a) 0.5 h, (b) 8 h and (c) 128 h of milling.

The sample of 256 h of milling was investigated by TEM to ascertain if besides crystalline material also amorphous material is present. With TEM three morphologies have been observed. Around 50% of the particles (typical agglomerate shown in Fig. 4) contain crystallites with sizes of approximately 12 nm, 30% crystallites with sizes of less than 2 nm and around 20% are amorphous. The milled powders were subjected to heating steps at 700 and 800°C to increase the crystallinity. According to XRD measurements the crystallinity of samples heated at 700°C is increased but the crystallinity of samples heated at 800°C did not much improve.

Wet chemical analyses revealed an iron content in the milled powder of 0.020 wt.%. Other main constituents (chromium, nickel) of the milling steel present in the milled powder are a factor 5–10 less than the iron content detected.

Sintered pellets of $BaTiO_3$ were prepared from powder, which has been milled for 256 h. Typically, a density of max. 92% of the theoretical value was achieved even for sintering temperatures of up to 1350°C. SEM investigations of sintered pellets showed an inhomogeneous microstructure with areas which are partly very dense and areas which show some porosity. The typical grain size in the denser areas is about 0.1–0.2 μm as shown in Fig. 5. Dielectric measurements on pellets sintered at various temperatures are shown in Fig. 6. This shows that the dielectric properties do no change much for sintering at 1250°C and higher. Due to the relatively high porosity and the small grain size the dielectric constant is low. Furthermore, experiments in which the

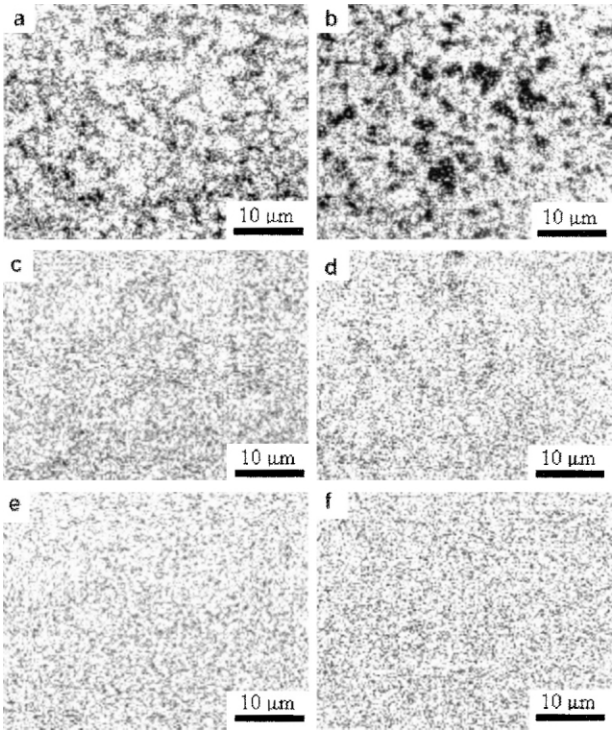

Fig. 3. EPMA mappings of $BaTiO_3$ samples milled for (a,b) 0.5 h, (c,d) 8 h and (e,f) 128 h. Ba-mapping (a,c,e) and Ti-mapping (b,d,f).

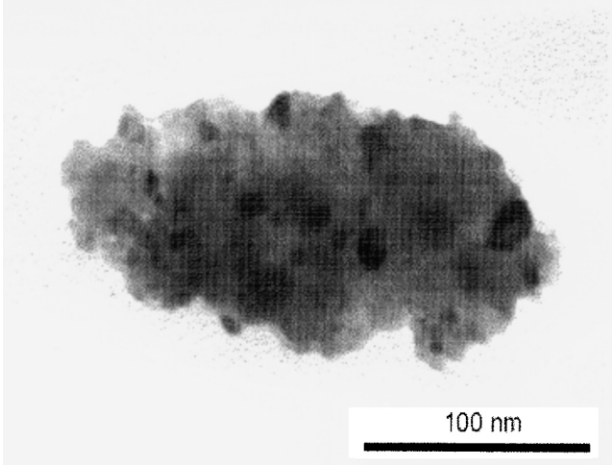

Fig. 4. TEM micrograph of $BaTiO_3$ powder after 256 h of milling.

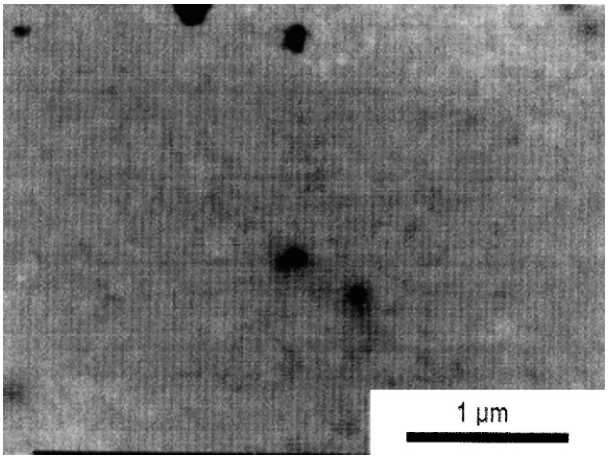

Fig. 5. SEM micrograph of $BaTiO_3$ pellet sintered for 1 h at 1350°C.

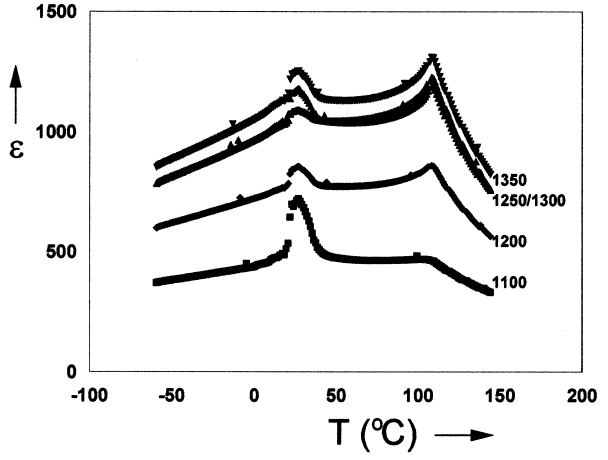

Fig. 6. Dielectric constant of $BaTiO_3$ pellets sintered at various temperatures.

Ti/Ba ratio (B/A ratio) is optimised, are expected to improve the dielectric properties.

3.2. $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$

For the preparation of $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ the same procedure is used as for $BaTiO_3$. XRD measurements on the composition $Bi_{0.5}Na_{0.5}TiO_3$, milled for 166 h, revealed single phase $Bi_{0.5}Na_{0.5}TiO_3$ (Fig. 7). The composition $Ba_2NaNb_5O_{15}$, milled for 168 h, showed only phase $Ba_2NaNb_5O_{15}$ besides an amorphous background (Fig. 8), which was not improved when further milled. For $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ wet chemical analyses revealed an iron content of respectively 0.048 wt.% and 0.069 wt.%.

Heating at 800°C showed an improved crystallinity of the as-milled materials $Bi_{0.5}Na_{0.5}TiO_3$ (Fig. 7) and $Ba_2NaNb_5O_{15}$ (Fig. 8). These powders have been used for the sintering of pellets for dielectric measurements.

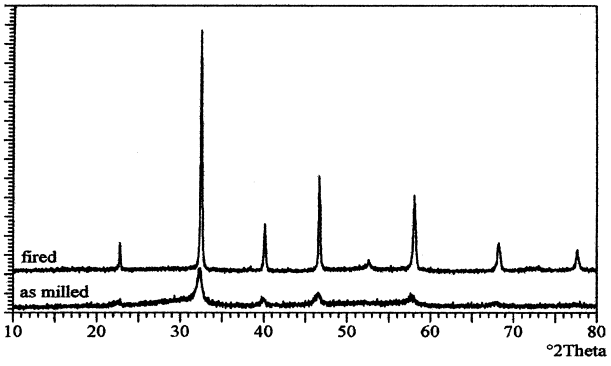

Fig. 7. XRD patterns of as milled and subsequently fired for 2 h at 800°C $Bi_{0.5}Na_{0.5}TiO_3$.

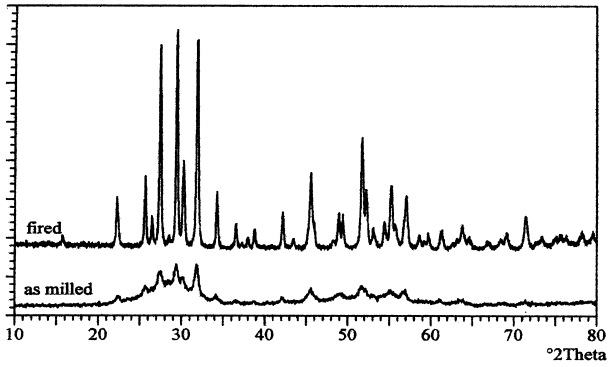

Fig. 8. XRD patterns of as milled and subsequently fired for 2 h at 800°C $Ba_2NaNb_5O_{15}$.

The density of pellets obtained for $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ when heated for 1 h at 1300°C are respectively 93.3 and 93.6% of the theoretical value. For $Bi_{0.5}Na_{0.5}TiO_3$ the dielectric constant at 25°C is 750 with a tgδ of 5%. The Curie point is 300°C at which ε is 3600. The particle size estimated from SEM micrographs is 10–20 μm. For $Ba_2NaNb_5O_{15}$ the dielectric constant at 25°C is 225 with a tgδ of 0.6%. The Curie point is 485°C at which ε is 580. The particle size estimated from SEM micrographs is 3–4 μm.

4. Conclusions

Mechanochemical synthesis is a promising technique for preparing compounds at low temperatures. The milling process results in powders with crystallite sizes in the nanometers range. Also partly amorphization might occur. The compounds $BaTiO_3$, $Bi_{0.5}Na_{0.5}TiO_3$ and $Ba_2NaNb_5O_{15}$ are prepared. Sintered ceramics of these powders show a relatively low density, even when sintered at high temperatures. These ceramics show poor dielectric properties, due to the not optimised B/A ratio, density and homogeneity.

Acknowledgements

H.J. Wondergem and H.-D. Bausen are acknowledged for XRD measurements, M.M.M.M. Vervest for SEM/EPMA analyses, M.A. Verheijen and M. Kaiser for TEM analyses and H.A. Troost-de Jong for wet chemical analyses.

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