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Synthesis of size controlled phase pure $KNbO_3$ fine particles via a solid-state route from a core–shell structured precursor

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Abstract

From a core–shell structured precursor, comprising Nb_2O_5 core enveloped by $KHCO_3$ in an equimolar proportion, phase pure $KNbO_3$ (KN) fine particles were obtained by calcining in air at 600 °C for 1 h. Disintegrating the large agglomerated particles of $KHCO_3$ prior to the precursor preparation enabled the micronization of the KN particle size down to 240 nm, close to that of the starting Nb_2O_5, due to increased mixing homogeneity and consequent thorough enveloping of individual Nb_2O_5 particles. Based on these findings, together with the known coupling diffusion mechanism of potassium and oxygen into Nb_2O_5, it was concluded that the core–shell particles in the precursor serve as a separated reaction space to complete the formation of KN without appreciable coalescence or local sintering, as far as the firing temperature is low enough like those employed in the present study. Superiority of $KHCO_3$ over K_2CO_3 or KNO_3 as a potassium source was also discussed.

Keywords: $KNbO_3$; Core–shell structure; Low temperature synthesis; Solid state reaction

1. Introduction

$KNbO_3$ (KN) is regarded as one of the most promising lead-free piezoelectric materials to replace $PbZrO_3$–$PbTiO_3$ (PZT) [1–3], for the application to actuators, in particular [3,4]. Stability at around the room temperature imparts KN another attractive point, since its Curie temperature is as high as 418 °C [5]. Preparation of KN powders via a hydrothermal route is one of the frequently applied methods [6–9]. A sol–gel method is an alternative to the hydrothermal route [10–13]. Heating by microwave was also reported [14].

However, most of these new methods are time consuming with lower productivity as compared to the solid state processes. The latter becomes even more beneficial, when the particle size distribution of the final product could be predicted from the states of the starting mixture, prior to firing. With the advent of fine powdered oxide particles available at a reasonable cost, we may now seriously reconsider the industrial affordability of the solid state processes for high valued electroceramic powders [15–17].

There are, however, difficulties to synthesize KN powders via a solid-state route [18–20], among others, to keep the stoichiometry, due to high hygroscopicity of the conventional potassium source, i.e., K_2CO_3, and high volatility of the potassium component at elevated temperatures necessary for reaction completion [18].

To surmount these obstacles, an appropriate choice of the potassium source, thorough mixing, and consequent decrease in the calcination temperature are essential. Use of potassium citrate is one of the potential possibilities [21]. Efforts were also paid to add urea to improve the reaction process [22]. The citrate method was indeed successful to decrease the reaction temperature. The particle size distribution was, however, rather broad and was not controllable.

In the present study, the authors try to reexamine the solid-state process leading to the phase pure KN fine powder particles by starting from a thoroughly mixed precursor. Efforts were paid to keep the homogeneity and stoichiometry of the starting mixture, by evaluating their states prior to firing, and to select

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appropriate potassium source. All these are directed toward the goal, to obtain phase pure KN fine powders with controlled particle size distribution.

2. Materials and methods

2.1. Sample preparation

Three species of potassium source, i.e. $KHCO_3$, K_2CO_3 and KNO_3, and a niobium source, Nb_2O_5, were used as purchased (Waco Pure Chemicals). Three grams of the stoichiometric mixture were subjected to vibration milling (Hi-Speed Vibrating Sample Mill, TI-100, CMT, Japan) with 60 g of nylon-coated steel balls, after a preliminary mixing in an agate mortar for 5 min. Preliminary disintegration of $KHCO_3$ agglomerates was done by vibration milling under the same condition. The starting mixtures were calcined in air by varying temperature up to 800 °C for 1 h.

2.2. Characterization

Mixing homogeneity of the particulates was examined by electron probe micro analyzer (EPMA, Shimadzu, EPMA-8705). X-ray photoelectron spectroscopy (XPS, JEOL, JPS-90SX) was used to examine the possible atomic interaction via changes in the binding energy of some core electrons, O 1s, Nb 3d and K 2p. Microstructure of the precursor was examined by transmission electron microscope (TEM, FEI, TECHNAI F20), equipped with the energy dispersive elemental analyses (EDXS).

Reaction processes upon heating was monitored by thermoanalyses (TG-DTA, MAC Science 2020), while the phase composition and cryastallographical properties were examined by conventional X-ray diffractometry (XRD, Rigaku, Rint-2200). Grain size and particle morphology of the starting mixtures and calcined products were observed by scanning electron microscopy (SEM, Hitachi, S-4700).

3. Results and discussion

3.1. Differences in the reaction products

X-ray diffractograms of the calcined products are compared in Fig. 1 between two potassium sources (a) $KHNO_3$ and (b) K_2CO_3, both starting from a mixture preliminarily vibro-milled for 1 h. Phase pure KN was obtained by calcining at above 600 °C. As far as XRD is concerned, no significant differences were observed between the starting potassium sources.

Particle morphology of the calcined products is, however, quite different. As shown in Fig. 2(a), the powders obtained from $KHNO_3$ are fairly homogeneous and well dispersed, whereas those from K_2CO_3 exhibit large aggregates (Fig. 2(b)). When $KHNO_3$ agglomerates were preliminarily disintegrated, the particles of the calcined products, KN, were well dispersed with significantly smaller average particle size (Fig. 2(c)), being close to that of starting Nb_2O_5. This will further be discussed later on.

3.2. Difference in the reaction processes

Reaction processes monitored by TG-DTA are displayed in Fig. 3. No significant difference was observed by starting either from $KHCO_3$ or K_2CO_3 to reach the final stage of the reaction. This is understandable, in view of the reaction scheme

$$2KHCO_3 \rightarrow K_2CO_3 + H_2O + CO_2 \quad (1)$$

$$K_2CO_3 + Nb_2O_3 \rightarrow 2KNbO_3 + CO_2 \quad (2)$$

Starting from $KHCO_3$ implies its partial decomposition to K_2CO_3, while the latter stage, reaction (2), is common to both potassium sources. However, a careful observation of the TG curve reveals a slight weight gain in the case of K_2CO_3 at the beginning of heating. This is a consequence of water absorption, due to the highly hygroscopic nature of K_2CO_3,

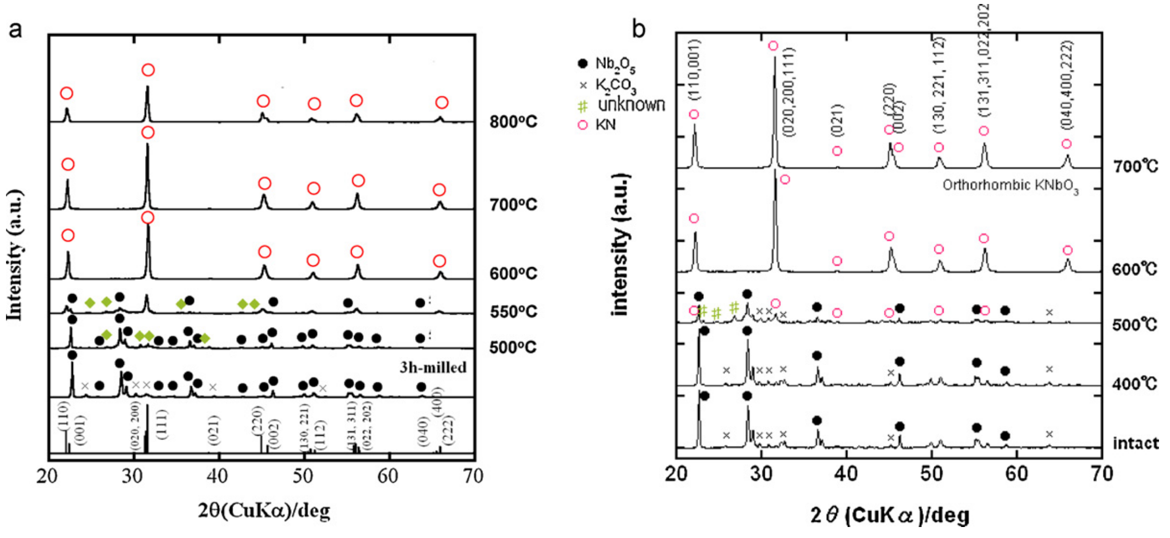

Fig. 1. X-ray diffractograms of the calcined products from (a) $KHCO_3$ and (b) K_2CO_3.

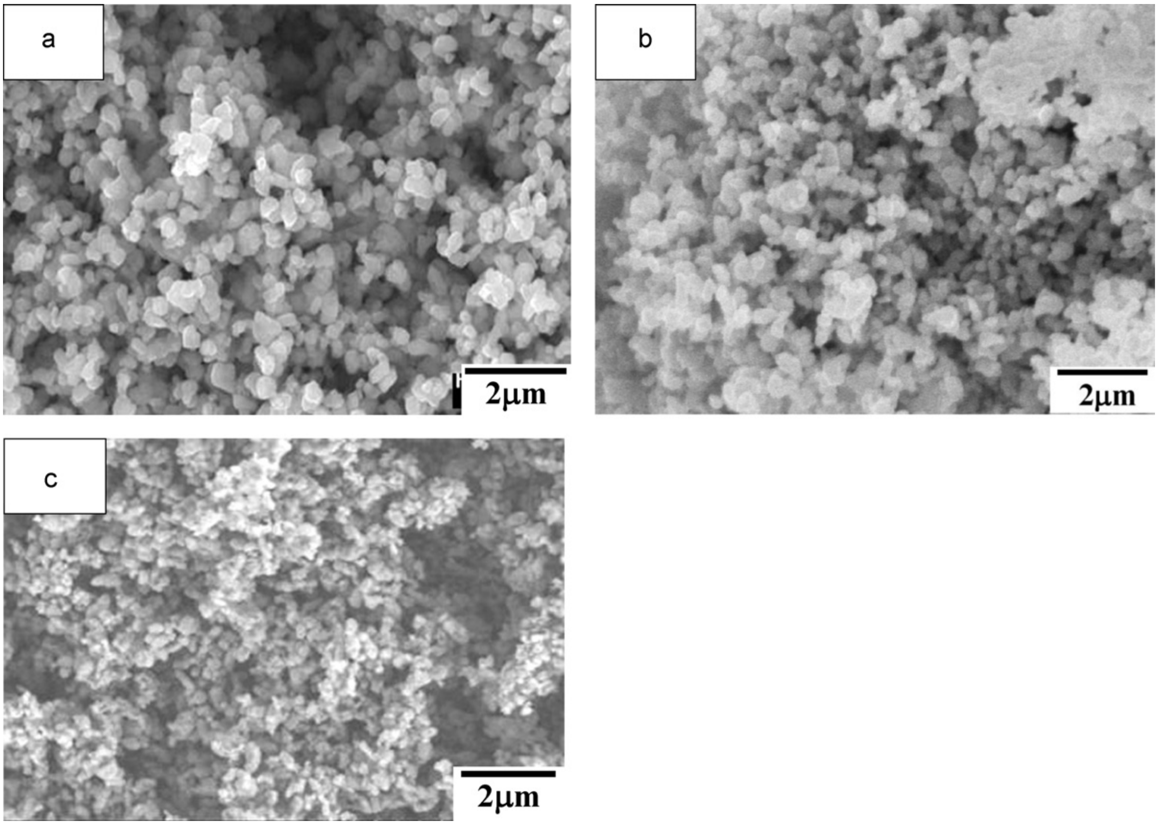

Fig. 2. Scanning electron micrographs of the calcined products from (a) $KHCO_3$, (b) K_2CO_3, and (c) $KHCO_3$, preliminarily disintegrated for 1 h.

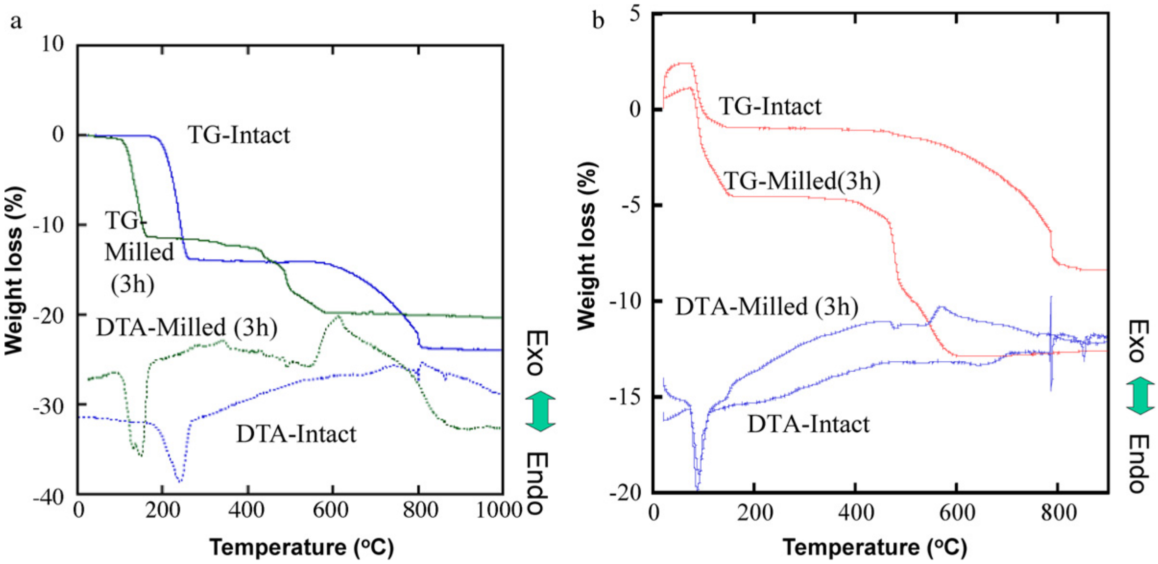

Fig. 3. TG-DTA profiles of the samples from (a) $KHCO_3$ and (b) K_2CO_3.

which easily leads to the undesired off-stoichiometry prior to heating.

3.3. Micromorphology and homogeneity of the reaction mixture

Mixing homogeneity of the starting mixtures or precursors on the particulate level was evaluated by EPMA. As shown in Fig. 4(a), the mixture starting from $KHCO_3$ exhibits concentration area for potassium was less than a few μm. In contrast, in the case of starting from K_2CO_3, we occasionally observe the high concentration area of potassium with its linear size more than 20 μm, as shown in Fig. 4(b). The difference in the homogeneity between $KHCO_3$ and K_2CO_3 is ascribed to the severer agglomeration of K_2CO_3, in line with the micrographic observation illustrated in Fig. 2.

XPS profiles are shown in Fig. 5 for the samples with $KHCO_3$. It is noteworthy that the Nb 3d signal weakened after

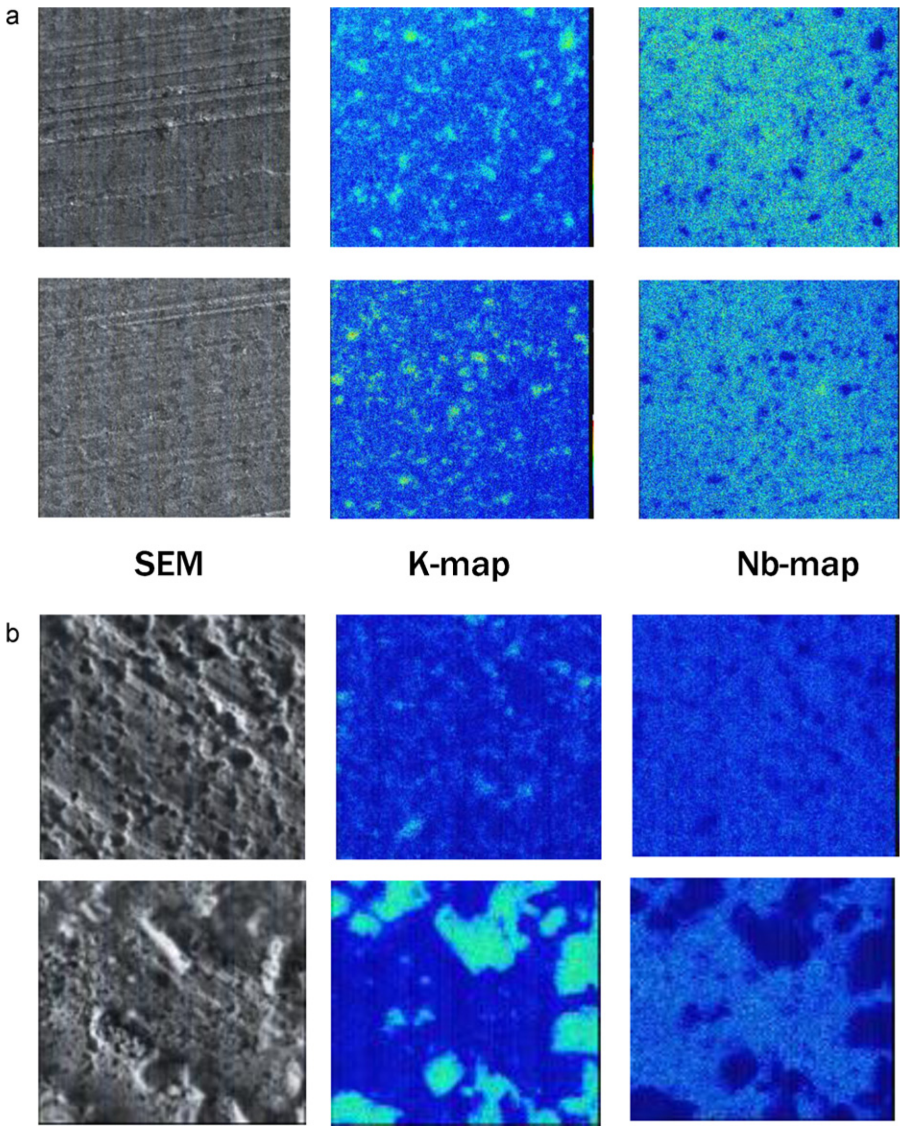

Fig. 4. EPMA mapping of the vibro-milled mixture, starting from (a) $KHCO_3$ and (b) K_2CO_3. Two rows represent two different spots on the same sample. The entire width of each image is ca. 100 μm.

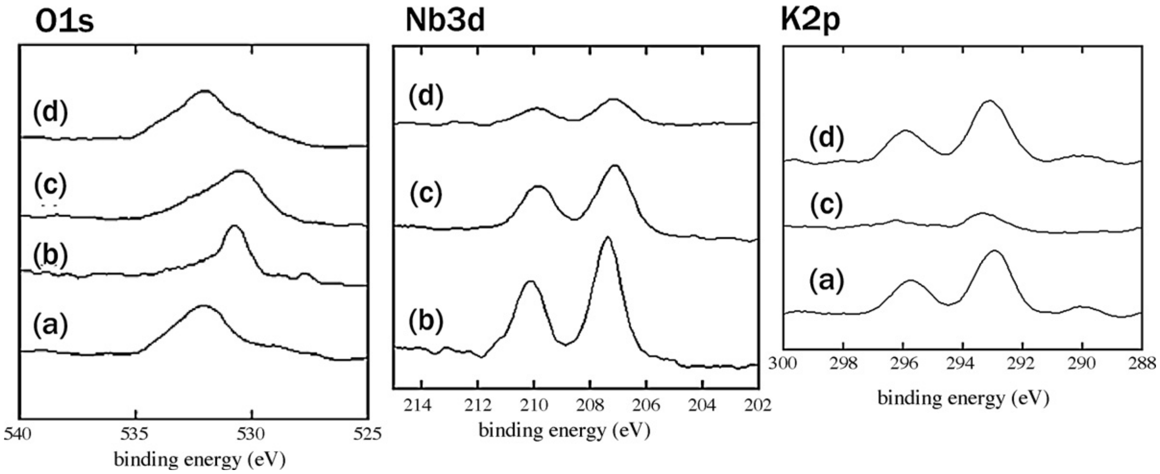

Fig. 5. XPS profile of O 1s, Nb 3d and K 2p. Common keys: (a) $KHCO_3$, (b) Nb_2O_5, (c) $KHCO_3 + Nb_2O_5$ as hand mixed, (d) the mixture after vibro-milling for 3 h.

vibro-milling, while the intensity of the K 2p signal increased, so that the effect of milling was quite opposite between Nb 3d and K 2p. In order to elucidate these changes, we observed the particle morphology under the scanning and transmission electron microscopes.

As shown in the SEM image in Fig. 6a, the finer particles of Nb_2O_5 are surrounding the much larger particles of $KHCO_3$. Arrows in Fig. 6a indicate $KHCO_3$ large particles, serving as substrates, on which tiny Nb_2O_5 particles are scattered. After vibro-milling for 3 h, the morphology drastically changed, as shown in Fig. 6b, where we observe the particles mostly less than 1 μm, with occasional agglomerates up to ca. 5 μm. Closer observation under TEM revealed the core–shell morphology, as shown in Fig. 6c, where each small particle is covered by a thin layer up to ca. 20 nm thick.

3.4. Core–shell structured precursor

We further examined the change in the local composition with the aid of EDXS. A line scanning of the Nb–L, Nb–K and K–K signals clearly revealed the high concentrations of potassium in the near surface region and of niobium in the interior of the particle, as shown in Fig. 7. This explains the structure of the core–shell, i.e. Nb_2O_5-core enveloped by the $KHCO_3$ shell. The changes in the XPS signals by vibro-milling are quite compatible with the present microscopy, coupled with the EDXS analysis. Before vibro-milling, the finer Nb_2O_5 particles simply cover the surface of $KHCO_3$. Therefore, the near surface Nb concentration is relatively higher than the average stoichiometry. During vibro-milling the mixture, $KHCO_3$ deformed plastically, surrounding the harder Nb_2O_5 particles and increasing the relative intensity of K 2p signals in the near surface region. Thus, the core–shell structure has most likely been formed under the shear stress exerted by a vibro-mill due to the substantial difference in their plasticity.

According to Szot et al. [23] and Malic et al. [24], the formation of KN proceeds by the coupled diffusion of potassium and oxygen ions into niobium oxide. It is therefore reasonable to assume that the particle size of the product KN is predominated by that of Nb_2O_5. As we tried to mechanically disintegrate the large aggregated particles of $KHCO_3$ by vibro-milling, we observed the micronization of the product, KN, which was close to that of the starting Nb_2O_5. The result is interpreted in terms of the core–shell structure mentioned above, by assuming that each KN particle is formed within a core–shell unit, serving as a micrometric-reaction space. Further particle growth or coalescence of KN was prevented due to low enough calcination temperature, i.e. at 600 °C. Preliminary disintegration of $KHCO_3$ enables its better distribution throughout the mixture, and hence, thorough

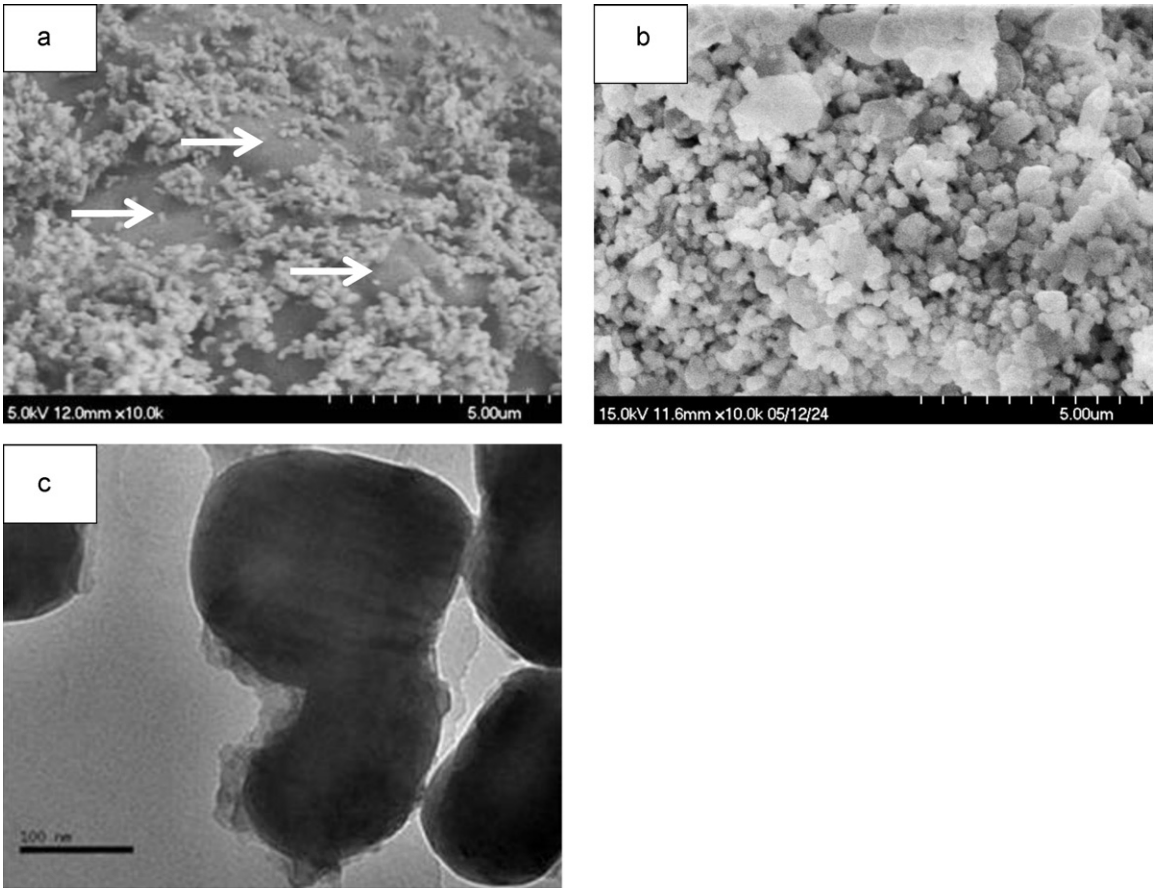

Fig. 6. Micrographs of the mixture (a) SEM before vibro-milling (arrows indicate $KHCO_3$ large particles serving as substrates, on which tiny Nb_2O_5 particles are scattered), (b) SEM after vibro-milling, and (c) TEM after vibro-milling. In images b and c, Nb_2O_5 particles were coated by $KHCO_3$.

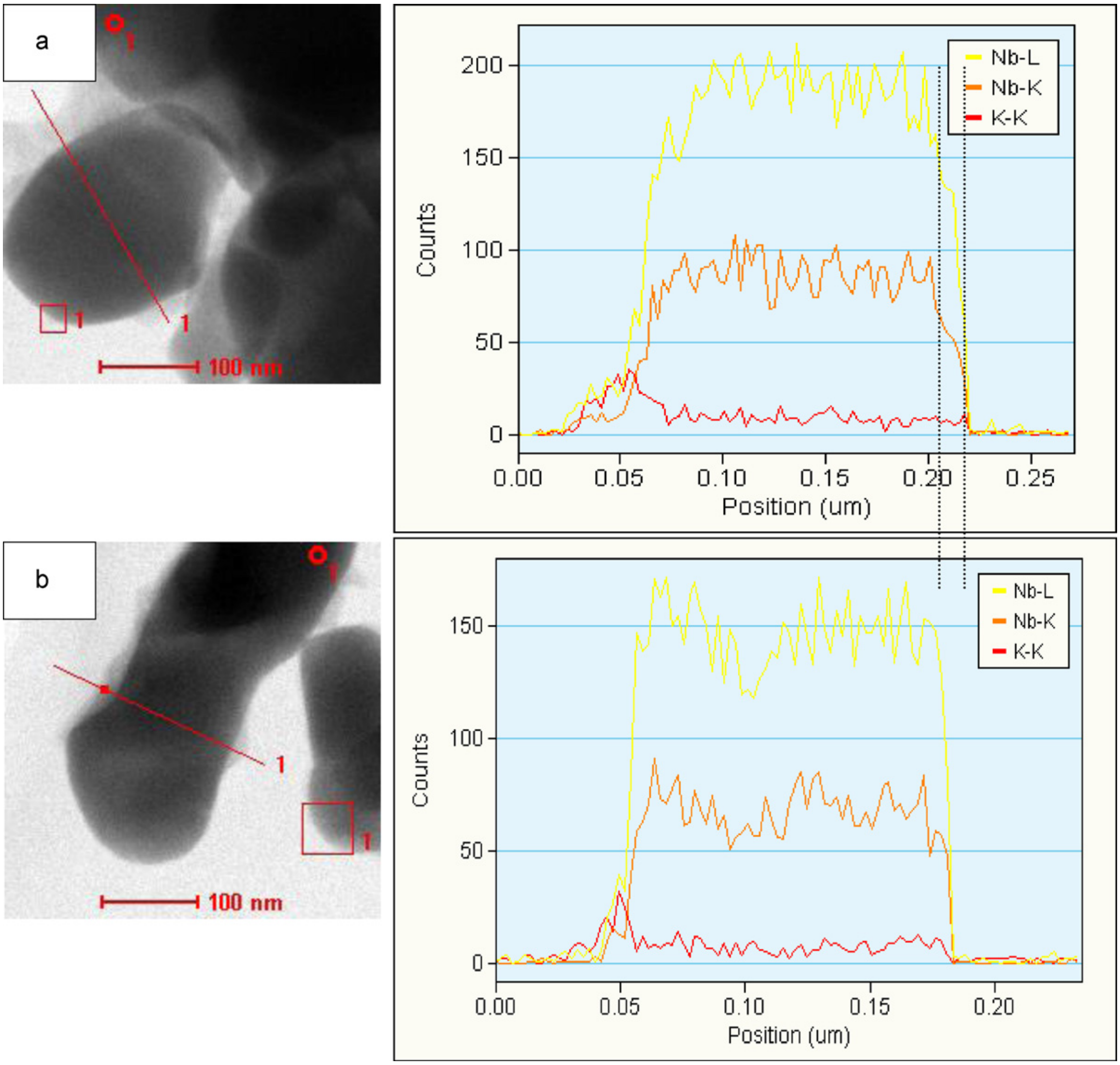

Fig. 7. Line profile of Nb and K by EDXS.

enveloping of individual Nb_2O_5 primary particles, and, accordingly, the particle size distribution of KN became closer to that of Nb_2O_5 primary particles. Under this hypothesis, we may expect that the particle size of the final ceramic product could be predicted by the starting particles size of the "core" materials, as far as the starting mixture comprise core–shell reaction units. The preliminary disintegration of $KHNO_3$ was favorable for more thorough enveloping of the individual Nb_2O_5 primary particles.

3.5. Reactions via a liquid phase

In order to explore even more homogeneous reaction space, we tried to use KNO_3 as a potassium source, which exhibits a clear melting point at around 330 °C, being much lower than its decomposition commencement, at around 600 °C, as shown in Fig. 8. It is also shown that the effect of the thorough mixing by vibro-milling is negligible, due to the emersion of the liquid phase. As shown in Fig. 9, the morphology of the phase pure KN, obtained by calcining the mixture at 700 °C, is entirely different from those starting from K_2CO_3 or $KHCO_3$, with a

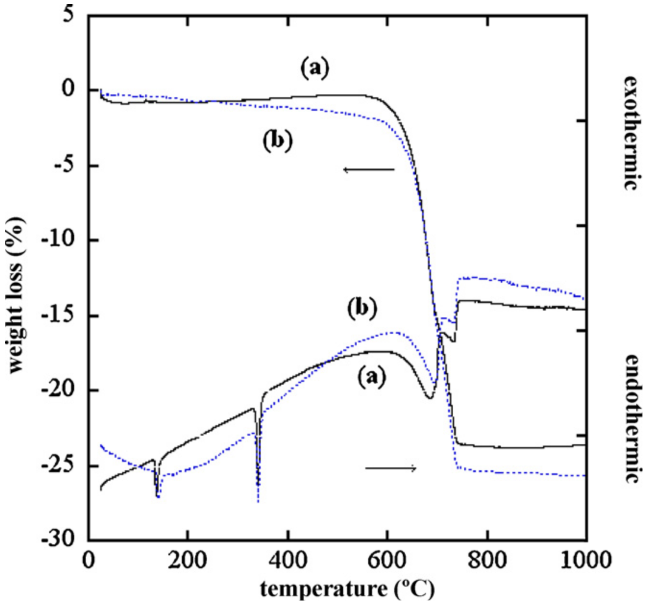

Fig. 8. Thermograms of the mixture KNO_3–Nb_2O_5 (a) before and (b) after vibro-milling.

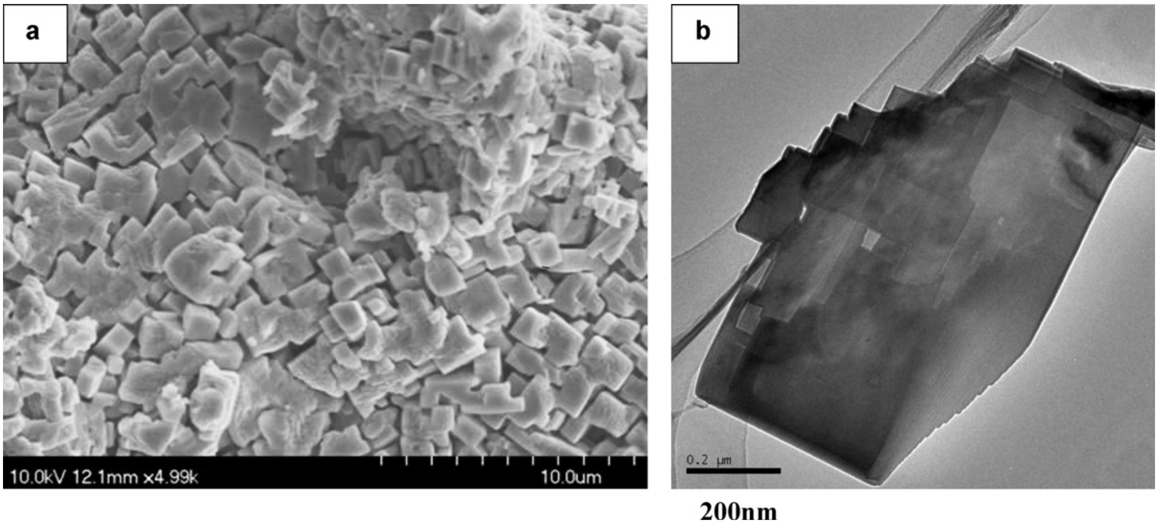

Fig. 9. Morphology of KNO_3 derived KN particles.

well developed crystal habit. These products may be used for different purposes, but are not in line with the present goal of obtaining phase pure micro particles with controlled particle size distribution.

4. Conclusions

In an attempt to obtain fine, phase pure $KNbO_3$ (KN) fine powder particles, effects of thorough mixing of the starting ingredients were examined with three different potassium sources, i.e. $KHCO_3$, K_2CO_3, and KNO_3 combined with a common reaction partner, fine grained Nb_2O_5. Superiority of $KHCO_3$ over K_2CO_3 became obvious to avoid hygroscopic nuisance and associated risk of off-stoichiometry, by avoiding serious aggregation of the products. From a core–shell structured precursor, comprising Nb_2O_5 core enveloped by $KHCO_3$ in an equimolar proportion, phase pure KN fine particles were obtained by calcining in air at 600 °C for 1 h. Disintegrating the large agglomerated particles of $KHCO_3$ prior to the precursor preparation enabled the micronization of the KN particle size down to 240 nm, close to the primary particle size of Nb_2O_5 due to increased mixing homogeneity and consequent thorough enveloping of individual Nb_2O_5 particles.

Based on these findings, together with the known coupling diffusion mechanism of potassium and oxygen into Nb_2O_5, it was concluded that the core–shell particle in the precursor serves as a separated reaction space to complete the formation of KN without appreciable coalescence or local sintering, as far as the firing temperature is low enough like those employed in the present study. Superiority of $KHCO_3$ over K_2CO_3 or KNO_3 as a potassium source was also discussed. Thus, the present core–shell precursor not only enables low temperature syntheses of phase pure KN, but also prediction of the particle size distribution of the final products from that of the starting core particle size.

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