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Mechanochemical synthesis of mangano-columbite ($MnNb_2O_6$) from manganese (II) oxide and niobium pentoxide

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ABSTRACT

A mixture of manganese (II) oxide (MnO) and niobium pentoxide (Nb_2O_5) was ground in air with a planetary ball mill to investigate the mechanochemical (MC) reaction between the two oxides. A subsequent thermal treatment was conducted at 600 °C to enhance crystalline quality. The intensive grinding enables us to form mangano-columbite ($MnNb_2O_6$) with an orthorhombic structure. This reaction proceeds with an increase in the grinding time and ultimately was almost completed within 120 min. By heating at 600 °C, the partially defective structure of $MnNb_2O_6$ that was mechanochemically synthesized can be changed into a good crystalline state, and this enhancement is improved by increased heating time. However, the crystallite sizes of $MnNb_2O_6$ are almost constant and are within the range of 30–50 nm.

1. Introduction

With the continuing proliferation of wireless communication technologies operating at microwave frequencies, there is an ever-increasing demand for cheap but nonetheless high-performance dielectric ceramics. One such application of microwave ceramics is as dielectric resonators, which have a resonant frequency (f_r) in the microwave region, typically between 1 and 10 GHz. To be effective dielectric resonator materials, these ceramics should have a sufficiently high relative permittivity to allow miniaturization of the component ($\varepsilon_r > 10$), low dielectric losses ($\tan\delta$) at microwave frequencies to improve electivity (quality factor, $Q > 5000$, where $Q \approx 1/\tan\delta$), and a temperature coefficient of resonant frequency as close as possible to zero for temperature stability ($\tau_f < \pm 20$ ppm/°C). Microwave ceramics are currently available with ε_r approximately 30–35, near-zero τ_f and $Q \times f_r = 150{,}000$–$300{,}000$ [1,2].

Among the materials investigated for use in dielectric applications, perovskites, such as $BaTiO_3$ or $PbZrO_3$, are the most popular and researched materials. However, the dielectric properties of certain columbites, binary niobates (ANb_2O_6; A = transition metal) in particular, have been surveyed in more recent studies [3–5]. In addition to their dielectric properties, these materials are known to have lower sintering temperatures than perovskites. In fact, relative densities greater than 95% can be more easily achieved. Moreover, regarding the structure, [Nb—O_6] octahedral groups share edges, forming chains along the *b*-axis, and this structure has been shown to allow antiferromagnetic interaction at low temperatures [6]. $MnNb_2O_6$ (manganocolumbites) especially are known as excellent microwave dielectric materials with excellent dielectric properties ($Q \times f_r = 343{,}000$ GHz, $\varepsilon_r = 22.4$ and $\tau_f = -59.6$ ppm/°C) [7–9].

Conventional solid phase reaction processes have generally been used for the preparation of ANb_2O_6 powders [10–17]. However, the powders obtained by solid-phase processes, which need to be run at high temperatures, have a large particle size. Especially on synthesizing $MnNb_2O_6$, it is necessary not only to heat at 1100 °C or over but also to control the atmosphere conditions carefully [18,19]. To prepare ANb_2O_6 powders suitable for sintering at low temperatures, several processes have been researched, such as (1) molten salt methods ($ZnNb_2O_6$, $MgNb_2O_6$) [20,21], (2) co-precipitation processes ($NiNb_2O_6$, $CoNb_2O_6$, $MgNb_2O_6$, $ZnNb_2O_6$, $CaNb_2O_6$, $CuNb_2O_6$) [22–26], (3) sol–gel processes ($NiNb_2O_6$, $MgNb_2O_6$, $ZnNb_2O_6$, $CdNb_2O_6$) [27–32], and (4) mechanochemical (MC) processes ($MgNb_2O_6$, $ZnNb_2O_6$) [33,34]. Each of them have some drawbacks, such as the requirement of removing alkali metals (K, Na) from the prepared powder (1), the need for pretreatment (dissolving Nb_2O_5 in 40% HF solution for 10 h), or complicated processing (2, 3). Conversely, MC processes can be much simpler procedures with a low cost, a lower operating temperature close to room temperature, and a requirement for widely available oxides as starting materials. Moreover, the MC process can produce

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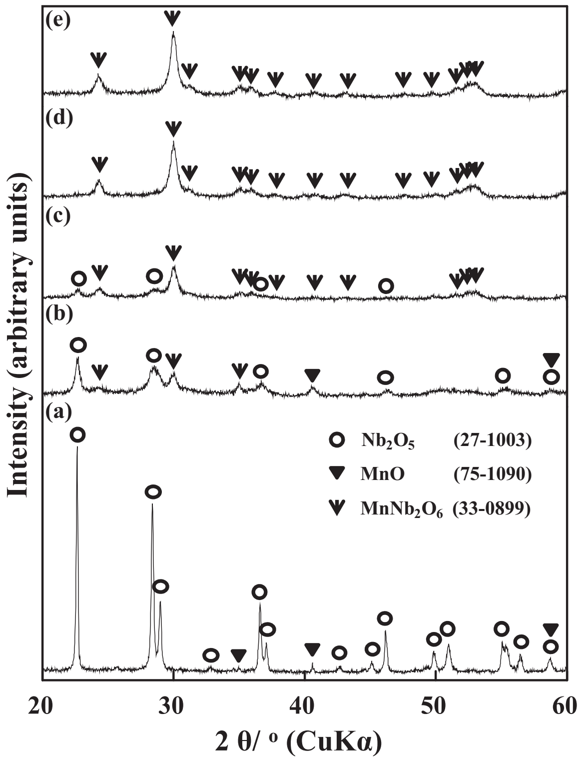

Fig. 1. XRD patterns of the MnO–Nb_2O_5 mixture ground for different periods of time: (a) no grinding, (b) 30 min, (c) 60 min, (d) 120 min, and (e) 180 min.

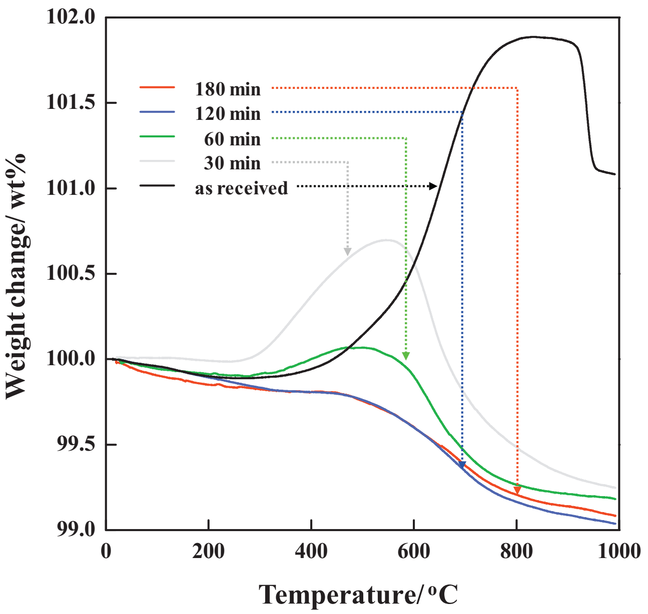

Fig. 2. TG analysis of the MnO–Nb_2O_5 mixture ground for different periods of time.

powders with nanometric sizes. However, there are few studies on MC synthesis of ANb_2O_6 and there is a paucity of information on the crystallographic properties of ANb_2O_6 synthesized by MC reactions.

The main purpose of this research is to provide information concerning the synthesis of ultrafine $MnNb_2O_6$ particles from MnO and Nb_2O_5 through a MC reaction and concerning the crystallographic properties of the reacted mixture.

2. Experimental procedure

Analytical grade niobium (V) oxide (Nb_2O_5, >99.0%, Merck Chemicals, KGaA, Germany) and manganese (II) oxide (MnO, 99%, Alfa Aesar Co., USA) were chosen as the starting materials. These materials were mixed at an equimolar ratio, and this mixture was kept in a desiccator. A planetary mill (Pulverisette-7, Fritsch, Germany) was used to grind the mixture. The mill is composed of a pair of pots made of zirconia installed on a rotating disc driven by an electric motor. Four grams of the mixture (MnO: 0.84 g, Nb_2O_5: 3.16 g) was put in the zirconia pot (45 cm^3 inner volume) with seven zirconia balls with a 15-mm diameter. The mixture was subjected to grinding in air at 700 rpm for various periods of time. The samples were characterized by high-resolution X-ray diffraction (HRXRD) analysis (X'pert-pro MPD, PNAalytical, Netherlands) using CuKα radiation (λ = 1.5406 Å) to identify the phases formed in the ground sample. The XRD patterns of the sample were recorded using a step size of 0.017° and a detection time of 10.34 s per step. To investigate crystal properties, Warren-Averbach and Rietveld analyses were carried out [35,36]. The thermal behavior of the mixture ground for various times was examined by thermogravimetric and differential thermal analysis (TG–DTA, SDT Q600, TA Instruments Ltd., USA) using a heating rate of 10 °C/min in air flow (100 ml/min) from room temperature up to 1000 °C. Powder morphology and microstructure were examined by transmission electron microscopy (TEM, JEM-2011 Luminography, Jeol, Japan) with selected area diffraction (SAD).

3. Results and discussion

Fig. 1 shows the XRD patterns of the MnO and Nb_2O_5 mixtures ground for various periods of time. Peaks of the two materials (MnO and Nb_2O_5) are observed in the XRD pattern of the as-received mixture (Fig. 1(a)). The peaks of the starting oxides decrease gradually with an increase in the grinding time. After grinding for 1 h, no peaks of MnO are detected in the pattern, although peaks of Nb_2O_5 can be observed. This indicates that MnO tends to change into a more activated state than does Nb_2O_5. Ultimately, all peaks of starting materials disappear in the mixture ground for 2 h. Conversely, new peaks of $MnNb_2O_6$ appear in the early stage of grinding within 30 min, and their intensity increases as the grinding progresses. In other words, MnO and Nb_2O_5 directly form a new crystalline structure. These peaks are consistent with the peaks of $MnNb_2O_6$ (orthorhombic, JCPDS No. 33-0899), and only peaks of $MnNb_2O_6$ are observed in mixtures ground for 2 h or more. Also, there are no noticeable differences in the XRD patterns of mixtures ground for 2 h or more. This result implies that $MnNb_2O_6$ can be synthesized by a MC reaction, and its structure can be sustained through intensive prolonged grinding.

Fig. 2 shows TG curves of the mixtures ground for different periods of time. These curves can be categorized into two groups: one is a group with a short grinding period (30 and 60 min) and the other is a prolonged grinding group (120 and 180 min). In the case of the untreated, as-received mixture, significant weight increase can be seen in the temperature range from 400 to 800 °C, reaching approximately 101.89 wt%. At higher temperatures, the weight decreases dramatically at 940 °C, reaching approximately 101.11 wt%. These results can be explained by the oxidation and reduction of manganese oxides. MnO will be oxidized slowly to Mn_2O_3 from 400 °C, and this Mn_2O_3 will be decomposed to Mn_3O_4 at 940 °C. The weight change of the mixture as received may result from the phase change of MnO [37], as described in Eqs. (1) and (2).

$$2MnO + 1/2O_2 \rightarrow Mn_2O_3 \quad (400\text{–}800\,^{\circ}C) \tag{1}$$

$$3Mn_2O_3 \rightarrow 2Mn_3O_4 + 1/2O_2 \quad (940\,^{\circ}C) \tag{2}$$

Nb_2O_5 and $MnNb_2O_6$ are stable, without reduction or oxidation, during thermal treatment to 800 °C in air. This finding implies that the weight change may result only from unreacted MnO. As for the former group, the weight gain can be also detected in the range of 300–600 °C. However, the initiation temperature of weight gain is marginally lower by approximately 100 °C than that for the untreated mixture. Also, the weight gains of the mixtures in the former group decrease in inverse proportion to the grinding time, reaching 100.70 wt% (for the mixture ground for 30 min) and 100.07 wt% (for the mixture ground for 60 min). Based on

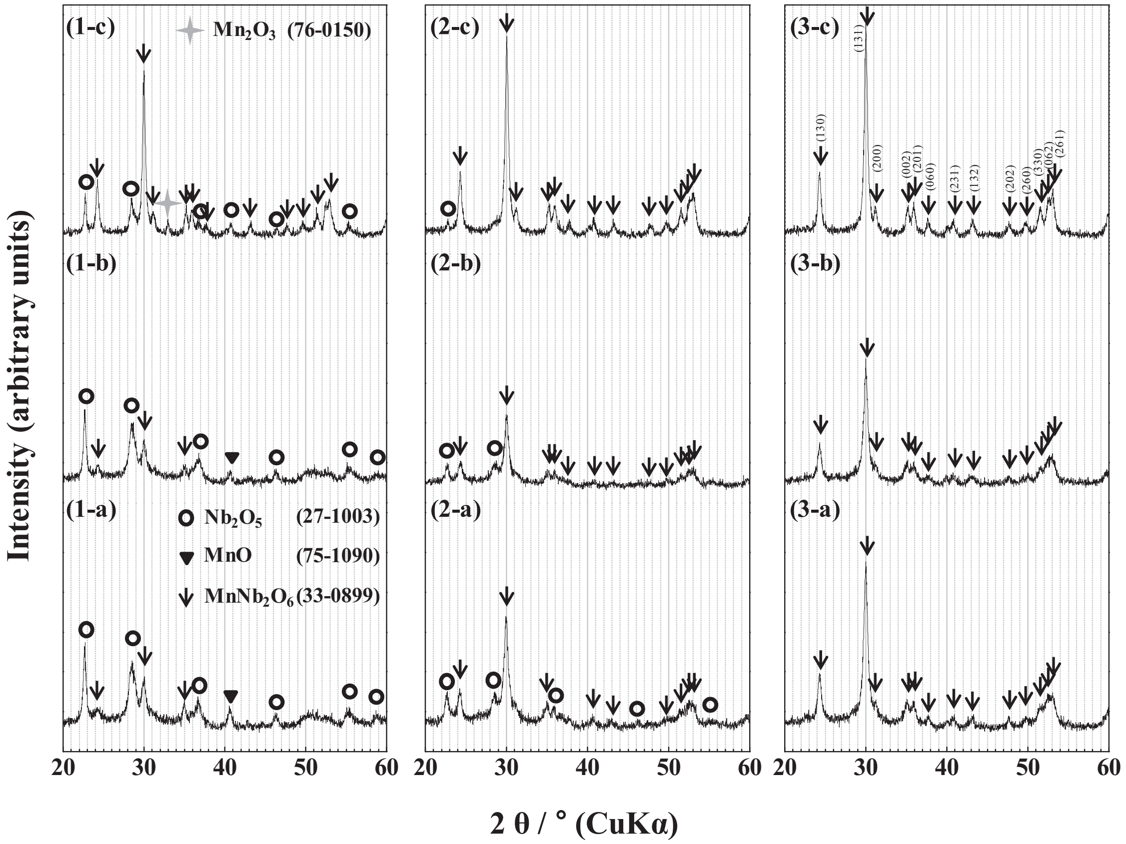

Fig. 3. XRD patterns of the MnO–Nb_2O_5 mixtures ground for different periods of time and of those heated at 300 and 600 °C for 2 h: (1) the mixture ground for 30 min, (2) for 60 min, (3) for 120 min, and (a) no heating treatment, (b) heating at 300 °C, and (c) at 600 °C.

calculation using Eq. (1), the amounts of unreacted MnO in the mixtures ground for 30 and 60 min are 29.4 and 2.9%, respectively.

Conversely, this weight gain cannot be detected in the latter group, regardless of grinding time. These results can be explained by a mechanochemical reaction between MnO and Nb_2O_5. The weight gain comes from the phase change of MnO, and the weight of unreacted MnO and the initiation temperature of weight gain both decrease as the reaction proceeds. Finally, unreacted MnO disappeared in the mixtures ground for 120 min or more. These results are consistent with Fig. 1.

In order to confirm these analyses, heating treatments were conducted with the ground mixtures. Generally, the compounds treated mechanochemically have structural defects, which would influence their XRD analysis [33,34]. In these cases, in order to detect even the minor compounds using an XRD analyzer, it is necessary to improve the crystal quality, and therefore annealing of the ground mixture at a relatively low temperature is conducted. In this research, annealing was conducted at 300 and 600 °C for 2 h. The XRD patterns of the annealing samples are shown in Fig. 3.

In the case of manganese oxide, the peak can be detected in the mixture ground for 30 min after heat treatment for 2 h at 300 and 600 °C, while the patterns of the mixture ground for 60 min or more have no peak of MnO, regardless of heat treatment at 300 or 600 °C. Especially in the mixture ground for 30 min and heat treated at 600 °C for 2 h, a new peak of Mn_2O_3 (cubic, 76-0150) can be detected in the pattern. This result is in accordance with the explanation for the TG results shown in Fig. 2. No detection of manganese oxides in the pattern may be due to their

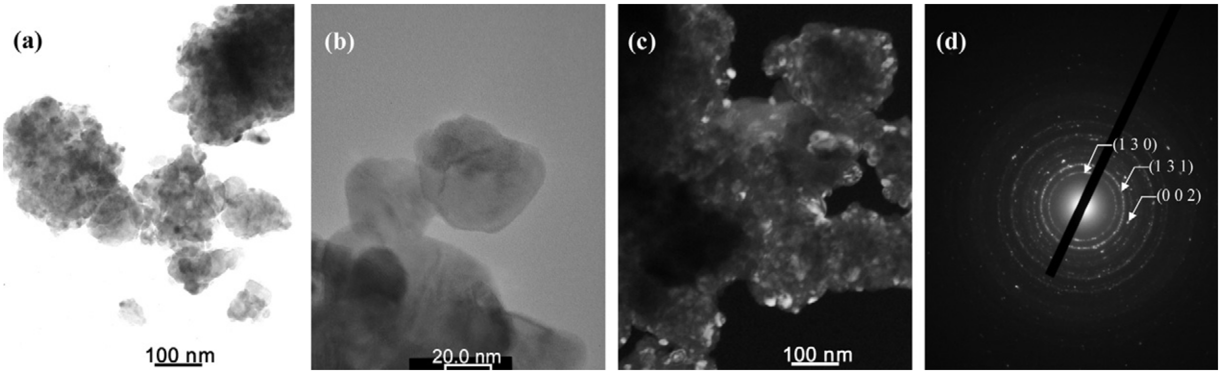

Fig. 4. Bright, dark field images and SAD pattern of the 120-min ground mixture treated at 600 °C for 2 h: (a, b) bright field images, (c) dark field image and (d) SAD pattern.

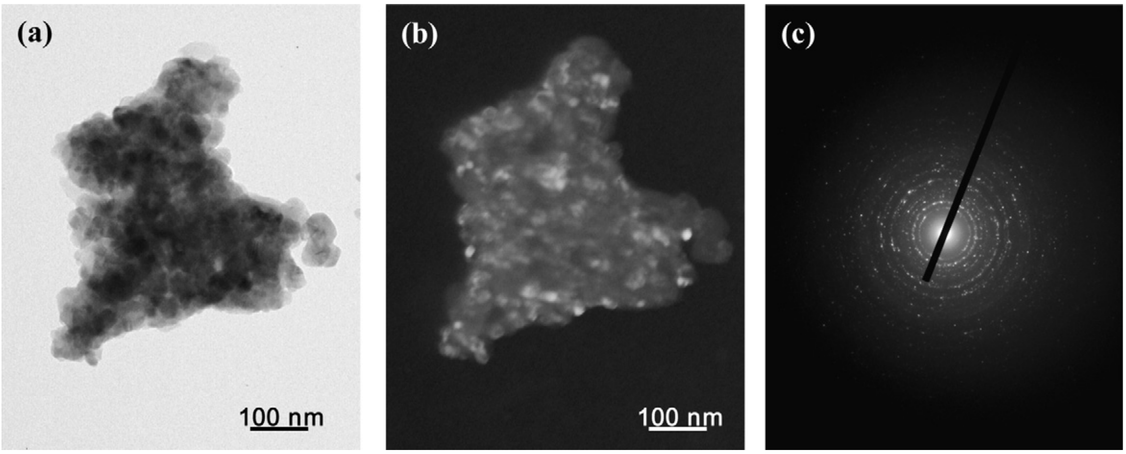

Fig. 5. Bright, dark field images and SAD pattern of the 120-min ground mixture treated at 600 °C for 10 h: (a) bright field image (b) dark field image and (c) SAD pattern.

infinitesimal portion in the mixture about 0.61 wt%, as calculated by Eq. (3).

$$\mathrm{MnO}_{\text{initial content in mixture, wt\%}} \times \mathrm{MnO}_{\text{unreacted proportion, \%}} = \mathrm{MnO}_{\text{unreacted residue in the ground, wt\%}} \quad (3)$$

The peaks of Nb_2O_5 are present in the pattern of the mixture ground for 60 min or less. The intensities of these peaks decrease with an increase in heating temperature, and the intensities of $MnNb_2O_6$ increase at the same time. This implies that $MnNb_2O_6$ can be synthesized from the mixture of MnO and Nb_2O_5 at temperatures below 600 °C, due to activation by intensive grinding. As for the mixture ground for 120 min, all peaks coincide with those of $MnNb_2O_6$, and their intensities increase in proportion to heating temperature.

To analyze the structural properties more delicately, the lattice parameters of Fig. 3(c) were refined in orthorhombic system by Rietveld analysis using TOPAS software (DIFFACplus, 2003) [38]. The lattice parameters of Fig. 3(c) (a = 5.731 Å, b = 14.287 Å, c = 5.093 Å) display very slight variations from those of JCPDS file numbers 33-0899 (a = 5.767 Å, b = 14.434 Å, c = 5.085 Å) [39]. c-Parameter increased by 0.16%, while a- and b-parameter diminished by 0.62 and 1.02%, respectively. These phenomena were reported in several reports [40–43]. It indicates that the expansion and shrinkage of lattice parameters depend on stressing manner of the particles during intensive grinding. That is to say, the expansion and the shrinkage of lattice parameter result from the grinding with loose media and compressive load, respectively.

Fig. 4 shows the results of TEM analysis for the mixture ground for 120 min and treated thermally at 600 °C for 2 h. As shown in the bright field images, the treated particles look like agglomerates (Fig. 4(a)), and their first-order particles are in the size range of 30–50 nm (Fig. 4(b)). The interplanar spacing calculated by ring pattern in SAD (Fig. 4(d)) for particles (Fig. 4(c)) is consistent with (1 3 0), (1 3 1), (0 0 2) of $MnNb_2O_6$ (orthorhombic) [39]. The TEM dark field image (Fig. 4(c)) indicates crystalline fine particles of $MnNb_2O_6$, dispersing in structural defective phase. Generally, particles of a material synthesized by mechanochemical methods are fine, and their crystal structures are largely disordered. Therefore, this partially defective phase of Fig. 4(c) is regarded as $MnNb_2O_6$ synthesized by a mechanochemical method. Through thermal treatment at 600 °C for 2 h, the outer structure can be improved crystallographically, while the inner structure remains unchanged. In addition, their sizes are almost constant, as shown in Fig. 4(c). This finding implies that a longer duration of the heat treatment at 600 °C can obtain good crystalline $MnNb_2O_6$, consisting of fine particles in the size range of several tens of nanometers. This statement is supported by additional TEM analysis of a ground mixture treated thermally at 600 °C for 10 h, as presented in Fig. 5. As shown in Fig. 5, the crystalline quality of $MnNb_2O_6$ powders synthesized by a mechanochemical reaction improves remarkably not only in the outer parts of the agglomerate but also in the inner parts. However, the crystalline size of $MnNb_2O_6$ remains in the range of 30–50 nm with little or no change.

4. Conclusions

Grinding a mixture of MnO and Nb_2O_5 in air with a planetary mill was conducted to synthesize mangano-columbite ($MnNb_2O_6$), and subsequent thermal treatment at 600 °C was conducted to enhance crystalline quality in the mixture that was ground for 120 min. The following conclusions can be made based on the experimental results:

1. $MnNb_2O_6$ can be synthesized mechanochemically by grinding the mixture, and the reaction proceeds with an increase in grinding time. The reaction is almost complete after grinding for about 120 min, and the product's structure can be sustained through intensive grinding.
2. Using TG analysis with the ground mixture, the amount of unreacted MnO may be evaluated quantitatively. The results are that the unreacted MnO decreases dramatically to 29.4% and 2.9% by grinding for 30 and 60 min, respectively.
3. Thermal treatment at 600 °C for the mixture ground for 120 min enables us to enhance the crystalline quality. With increasing heating time, the partially defective $MnNb_2O_6$ will be changed to a good crystalline state, though the crystallite sizes of $MnNb_2O_6$ are almost constant at a range of 30–50 nm.

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