



Phase Evaluation and Electromagnetic Properties of CoNb₂O₆ Columbite Material

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Abstract

CoNb₂O₆ was prepared by Chemical routes with alcohol as an additive. X-ray diffraction, Scanning electron microscopy and Transmission electron microscopy were used to investigate the lattice parameters and the particle morphology. The products were observed as irregular particles with an average particle size of ca. 500 nm, which agglomerated from thin slices. Compared with the common columbite CoNb₂O₆, which was obtained by a traditional solid-state reaction, the product obtained by the hydrothermal method crystallized into a rutile structure. The rutile CoNb₂O₆ was metastable and it could transform into the columbite structure after calcining at 800 °C in air for 4 h. Niobate compounds have been synthesized by columbite solid-state reaction method and characterized by X-ray diffraction (XRD), scanning electron microscope (SEM) and temperature as well as frequency dependence of dielectric and impedance study. Dielectric properties such as permittivity, dielectric loss, and temperature coefficient of resonant frequency are found to correlate strongly with the M-ions. The temperature coefficient of the resonant frequency may be correlated to the unit cell volume of MnNb₂O₆ among these compounds have very high quality factors.

Keywords:

Ceramics, Phase transformation, Oxides

1. Introduction

Divalent columbiteniobate ceramics with general formula MNb₂O₆ (M = Divalent cations) have very interesting characteristics as excellent dielectric property quality factor and temperature coefficient of resonant frequency [1-3]. These materials are very useful in human life. All materials have a high quality factor, ($\tan^{-1}\delta$). New composition developed for investigation dielectric properties. Dielectric properties such as permittivity (ϵ), quality factor, temperature coefficient of resonant frequency (τf) is still being developed. Studies in the field of niobate- and tantalite-based compounds have shown that AB₂O₆ (A=Co²⁺) with a columbite or rutile structure exhibits excellent performance in tests of magnetic, dielectric, thermoelectric and piezoelectric properties [1-6]. It is interesting that these compounds have a tremendous amount of potential for use as photo catalysts in the UV-visible region and can be used to investigate the photo catalytic properties of splitting water and organic compounds [3]. The products obtained by the SSR method often had a low active surface area and a wide particle size distribution. In the polymerized complex method and the sol-gel method, some expensive Nb sources were needed, such as NbCl₅ and Nb(OC₂H₅)₂. All of these factors prevented the development and mass-production of these niobates. There were some reports of hydrothermal synthesis under mild conditions, while most of the published studies were only concerned with the synthesis of alkali or alkaline-earth metal niobates (Na⁺, Mg²⁺, Ca²⁺, etc.) [10-13]. There were a few reports of transition metal niobates, especially the cobalt niobates [13]. Among these earlier reports, the most common structure of cobalt niobate was the columbite structure [5] and only one of these reports mentioned a particular cobalt niobate with a rutile structure. The rutile CoNb₂O₆ was prepared by the reaction of stoichiometric amounts of CoO and Nb₂O₅ powder in an argon atmosphere in temperatures up to 1400 °C. In 2007, a co-precipitation technique was used to prepare CoTa₂O₆ and CoNb₂O₆ [4]. The obtained CoTa₂O₆ crystallized in a rutile structure, but the CoNb₂O₆ crystallized in a columbite structure. Here, we report the synthesis of rutile CoNb₂O₆ based on a hydrothermal

process that uses polyvinyl alcohol (PVA) as an additive. The thermal stability of rutile CoNb_2O_6 was also studied by calcination at different temperatures ranging from 600 to 1000 °C.

1. Experiment

1.1. Synthesis

Nb_2O_5 (99.99%), $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ (99.0%) and KOH (99.0%) were used as the starting materials. All of the reactions mentioned below were conducted in a 50 mL stainless steel autoclave. A mixture of 0.550 g of Nb_2O_5 and 2.52 g of KOH was added to 35 mL of deionized water and this mixture was heated in the autoclave at 180 °C for 2 days. After cooling down naturally, a clear colourless solution of $\text{K}_8\text{Nb}_6\text{O}_{19}$ was obtained after removing the insoluble residue by centrifuging. A 4mL $\text{K}_8\text{Nb}_6\text{O}_{19}$ solution (0.0186 mol/L) was dissolved in 15 mL of 1-octanol, then 150 mg of polyvinyl alcohol (99.0%) was added. The pH value was adjusted to 7.0–7.5 with HCl solution. After being dissolved in 8 mL of deionized water, 65 mg of $\text{Co}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$ was added to an autoclave and thoroughly mixed until uniform. Ultimately, the autoclave was heated at 240 °C for 3 days. The products were centrifuged, washed with distilled water and dried under vacuum at 60 °C for 12 h.

2.2. Characterization

X-ray diffraction (XRD) experiments were carried out using a Rigaku D/MAX-2500/PC diffractometer with $\text{Cu} - \text{K}\alpha$ radiation at 40 kV and 200 mA and collected at 2θ angles of 10–80°. The products were observed using scanning electron microscopy (SEM) (JSM-6700F) and transmission electron microscopy (TEM) (JSM-3010).

2. Results and discussion

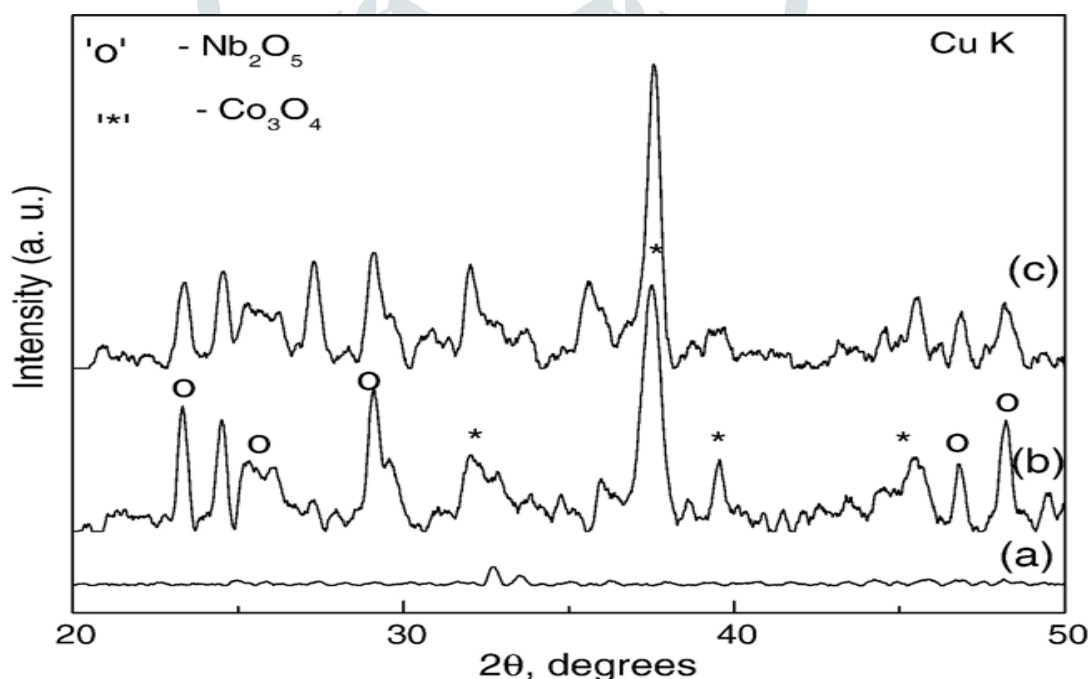


Fig. 1 XRD pattern of CoNb_2O_6 prepared at 240 °C

Fig. 1 shows the XRD pattern of CoNb_2O_6 prepared at 240 °C for 3 days. The marked peaks indicate that CoNb_2O_6 possesses a rutile structure, which was reported by Lahmann in 1980, rather than the common CoNb_2O_6 of columbite structure. The XRD pattern of this product is well indexed in the space group $\text{P}4_2/\text{mnm}$, which is in agreement with the JCPDS card No. 83–1798. The calculated lattice parameters by least squares fit are $a=b=4.726 \text{ \AA}$ and $c=3.054 \text{ \AA}$. The exact mechanism of the formation of the products with a Rutile structure in hydrothermal system is not clear. But it is common that the phases obtained in hydrothermal system are different from that obtained by conventional solid state reaction. The reaction mechanism of solid state reaction involves mainly the diffusion of atoms or ions at the interface between reactants, whereas the hydrothermal and solvothermal reactions involve the ions and/or molecules in solution.

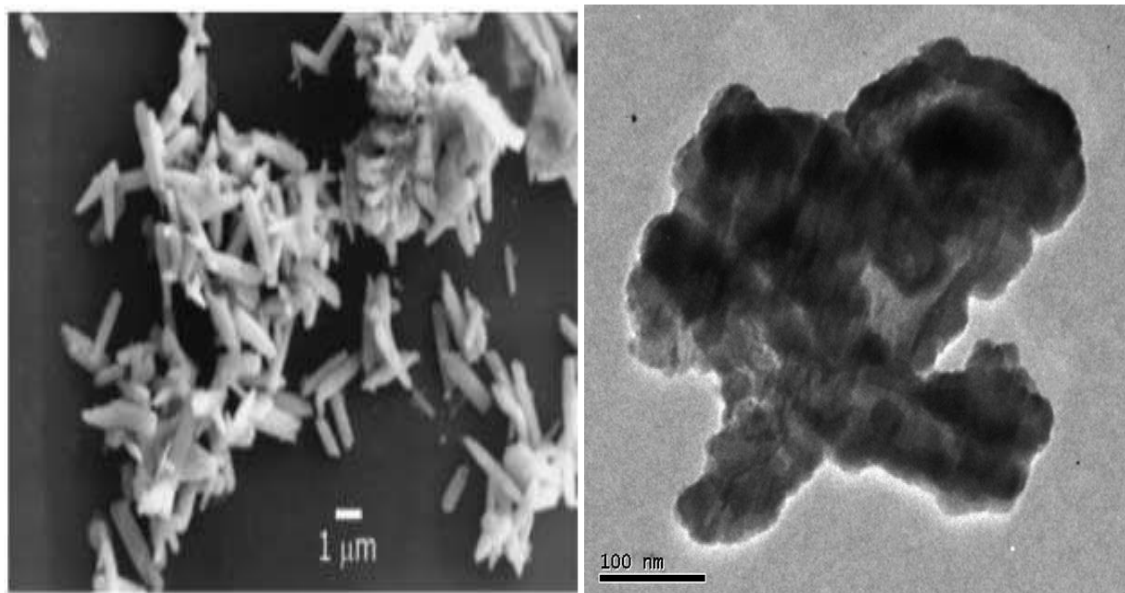


Fig. 2. SEM image of CoNb₂O₆ powders. TEM image of CoNb₂O₆ powders.

Fig. 2 shows the SEM and TEM images of the rutile CoNb₂O₆. Particles with an irregular morphology can be observed in the SEM images. The TEM images show that the particles were formed by the bagglomeration of thin slices. The diameter of a single particle is approximately 500 nm and almost all of the particles share the same particle size. The inset of Fig. 2D shows the SAED pattern of the thin slice, which confirms the rutile structure.

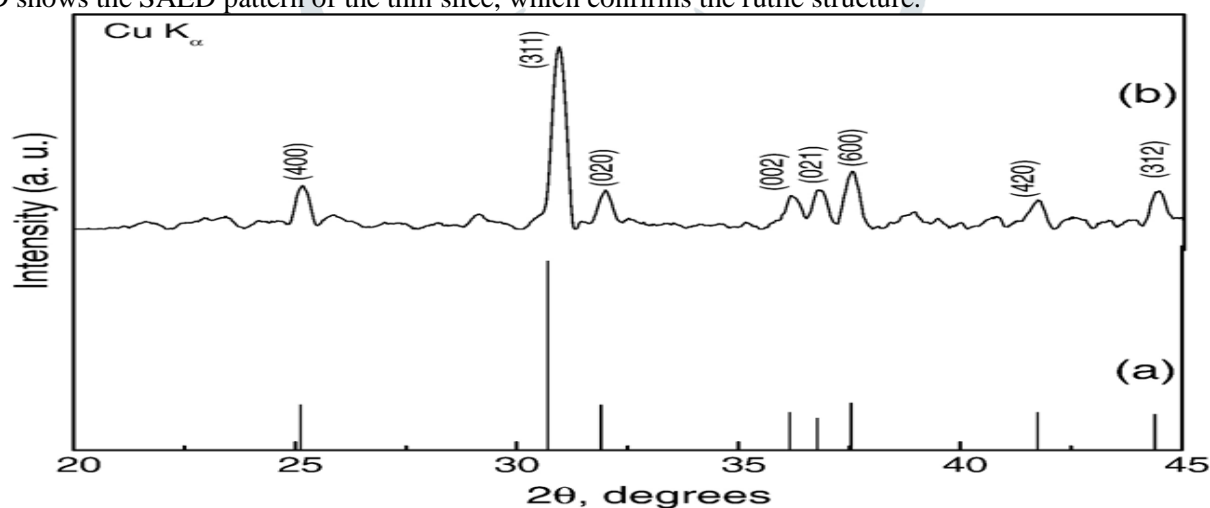


Fig. 3. (a) Ideal XRD pattern of CoNb₂O₆, (b) XRD of precipitate powders calcined at 700 °C.

Fig. 3 shows XRD patterns of the samples calcined at 600 °C, 700 °C, 800 °C and 1000 °C for 4 h in air, respectively. When the temperature was 600 °C, there was not much difference between the XRD patterns of rutile cobalt niobates and those of the calcined ones.

When we increased the calcining temperature to 700 °C, all of the characteristic peaks of rutile CoNb₂O₆ were weakened and some characteristic peaks of columbite CoNb₂O₆ appeared. When the calcining temperature was increased to 800 °C, all of the rutile CoNb₂O₆ was transformed into the common columbite structure. All of the d-lines of the crystal structure of columbite CoNb₂O₆ acquired at 800 °C matched the reported values (JCPDS: 32-0304), with lattice parameters of $a=5.710$ Å, $b=14.149$ Å and $c=5.043$ Å indicating a pure phase of the product. Rutile CoNb₂O₆ was also calcined at

4. Conclusions

A simple coprecipitation process was used for the preparation of ultrafine powders of CoNb₂O₆ at 700 °C. This is the lowest temperature reported for the formation of CoNb₂O₆ phase. Complex impedance analysis reveals both the bulk and grain boundary contribution, which are temperature dependent at higher frequency, behavior is almost temperature independent.

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