*Bulgarian Chemical Communications, Volume 50, Issue 3, (pp. 429 – 432) 2018*

# Sol-gel hydrothermal preparation of $Bi_4Ti_3O_{12}$ ceramic

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Received November 28, 2017; Revised May 15, 2018

This manuscript reports a modified method of preparation of $Bi_4Ti_3O_{12}$ ceramic powder by a sol-gel approach, followed by hydrothermal treatment of the obtained gel. Bismuth acetate and titanium isopropoxide were used as metallic sources to prepare the precursor gel, and it was successfully converted into bismuth-titanium oxide by hydrothermal treatment at 400 °C and 600 °C for 24 h. Multiple characterizations, namely XRD, FTIR, SEM measurements were used to validate the structural features.

**Keywords:** $Bi_4Ti_3O_{12}$; Sol-gel; Hydrothermal; Characterization.

## INTRODUCTION

Aurivillius oxides prepared through a soft chemical route such as hydrothermal or co-precipitation method attracts much attention. These methods constitute an environment-friendly medium for syntheses contrary to solid state methods, which need relatively high processing temperature (above 1100 °C).

Aurivillius phases have the general formula $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n+1})^{2-}$, where n=1-8, A stands for a divalent cation (*e. g*. $Ca^{2+}$, $Ba^{2+}$), B for a tetravalent or pentavalent ion (*e. g*. $Nb^{5+}$, $Ti^{4+}$) and form a perovskite block $A_{n-1}B_nO_{3n+1}$ [1]. The bismuth-titanium oxide $Bi_4Ti_3O_{12}$ belongs to this family with A=Sr, B=Ti and n=3. The bismuth layer-structured ferroelectric materials have attracted increasing attention for non-volatile ferroelectric random access memory (FeRAM) applications [2][3].

$Bi_4Ti_3O_{12}$ compounds have been prepared by various methods, which require more or less higher temperatures to be achieved. Preparation of powders by conventional processing, *i. e.* solid state reaction method (sintering temperature ~1150°C [4]), often leads to commotional and structural inhomogeneities in the produced ceramics. However, a sol–gel technology has been used to prepare $Bi_4Ti_3O_{12}$ nanopowders at ~900 °C [5]. A hydrothermal method has been developed for the synthesis of $Bi_4Ti_3O_{12}$ powder without treatment at high temperature [6,7].

To our knowledge, practical physical issues such as the structure-property relationship and the physical nature leading to the change of the properties for $Bi_4Ti_3O_{12}$ ceramics are not resolved, and from the viewpoint of physics there is lack of novelty. In this regard, this paper describes a novel method for synthesizing bismuth-titanium oxide. The effect of heat on sample' microstructure morphology was studied by XRD, FTIR and SEM.

## EXPERIMENTAL

The details of the sol-gel process used to prepare the appropriate alkoxide solution of bismuth and titanate have been published elsewhere [8,9]. A flowchart of the sol-gel procedure used is shown in Fig. 1. Stoichiometric amounts of a bismuth (III) acetate (Alfa, 99%) aqueous solution and a titanium (IV) isopropoxide (Sigma-Aldrich, 97%) solution stabilized by acetylacetone to form a titanium solution were mixed, and then dried to obtain a gel.

For hydrothermal treatment, the gel was kept under stirring in a solution of KOH (1 M) for 1 h, and then put into an autoclave (filling ratio above 80%) and heated at 180 °C for 12 h. After filtration and drying, the sample was thermally treated at 400 °C and 600 °C for 24 h.

The formation and quality of the powder were verified by X-ray diffraction (Philips X'Pert Pro). IR spectrum of the prepared powder at 600 °C was recorded on a Bruker, Vertex 70 DTGS FT-IR instrument using KBr pellet technique. Microstructure studies were performed by scanning electron microscopy with 10 kV of accelerating voltage at high vacuum.

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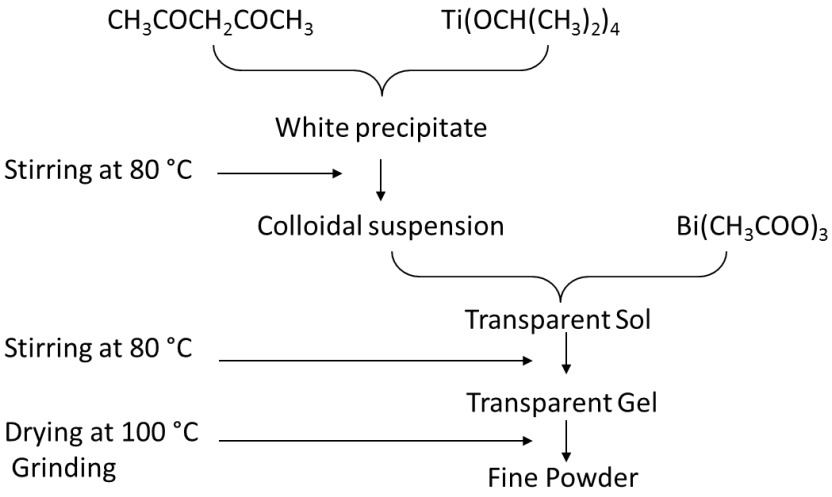


**Fig. 1**. Flowchart for preparation of powder by a sol-gel procedure.

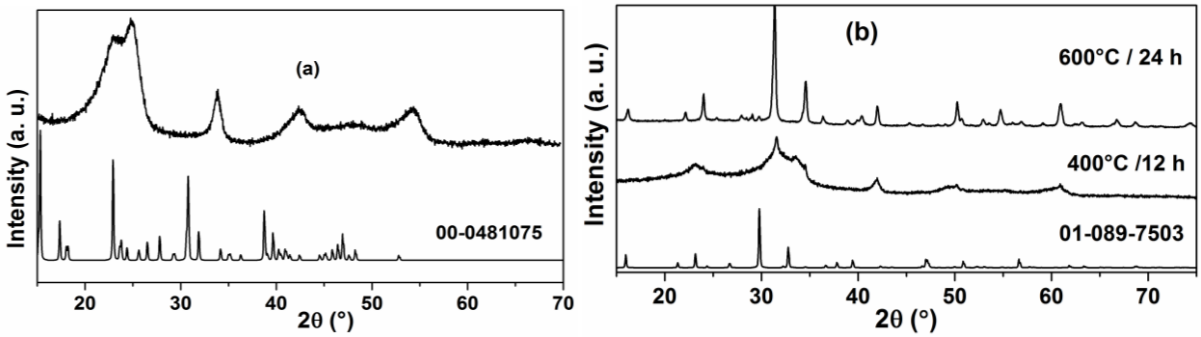


**Fig. 2.** XRD patterns of $Bi_4Ti_3O_{12}$ without (a) and with hydrothermal treatment (b).

## RESULTS AND DISCUSSION

Fig. 2 shows the X-ray diffraction patterns of dry gel (a) and ceramic powders obtained by hydrothermal treatment (b) of $Bi_4Ti_3O_{12}$. The XRD peaks were identified as bismuth acetate for the precursor gel before the hydrothermal treatment, according to the standard pattern $Bi(CH_3COO)_2$ (00-048-1075) (Fig. 2a).

The hydrothermally synthesized ceramic powders from the precursor gel at 400°C during 12 h were still quite amorphous, as expected. The XRD peaks became notably narrower with an annealing temperature of 600 °C for 24 h, indicating that this sample can be indexed using JCPDS-ICDD pattern number 01-089-7503 corresponding to $Bi_4Ti_3O_{12}$ tetragonal symmetry (space group $A2_1am$). As it can be seen from figure 3b, the XRD curves extracted using HighScore software of the sample annealed at 600 °C are remarkably similar to those obtained from the JCPDS-ICDD. However, the mismatch between the reference and experimental patterns is bigger than 0.05 2θ. This mismatch in peak positions may be explained by inaccuracies in the fitting software, offering inefficient curve fitting.

The average size for the sample sintered at 600 °C was estimated using Scherrer's formula:

$$D = \frac{0.9\lambda}{\beta cos\theta} \qquad (1)$$

where D is the crystallite size, λ the CuKα wavelength (1.5406 Å) and β the full width at half maximum (FWHM) [10], which was found to be 40 nm.

Fig. 3 shows the FTIR spectrum of the ceramic powder sintered at 600 °C. The bands at 3440 $cm^{-1}$ and 1633 $cm^{-1}$ are due to water molecules. The bands located at 23870 $cm^{-1}$ can be attributed to $CO_2$. The bands at 2853 $cm^{-1}$ and 2929 $cm^{-1}$ indicate the presence of residual organics. The band range 500-820 $cm^{-1}$ and the band at 936 $cm^{-1}$ are related to the crystallization of the phase $Bi_4Ti_3O_{12}$ [6.7]. The SEM micrographs of $Bi_4Ti_3O_{12}$ ceramic are shown in Fig. 4. The tow images taken at different locations, consist of plate-like and rod-like grains with random distribution comparing to plate-like morphology which is characteristic of the Aurivillius type [10–13]. The obtained samples are micro- to nanograined and contain, therefore, very developed grain boundaries and free surfaces. It has been recently demonstrated that the physical

properties of pure and doped fine-grained oxides strongly depend on the presence of defects like interphase boundaries and grain boundaries [14,15].

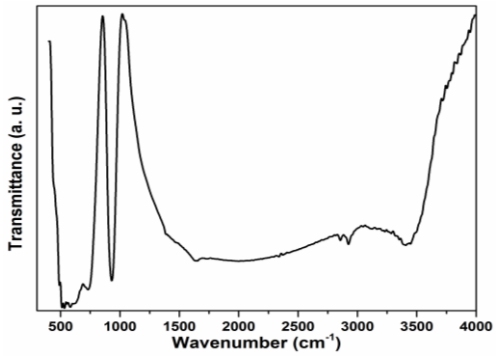


**Fig. 3.** FTIR micrograph of $Bi_4Ti_3O_{12}$ ceramic powder.

There is a high degree of inhomogeneity in size and shape of grains, and the average particle size is 1 μm – 0.2 μm. Thus, the hybrid hydrothermal – co-precipitation process can be used for manufacturing ultrafine-grained materials, differently from the solid-state method, which shows microcrystalline grains of plate-like shape.

The crystallite size (40 nm) estimated from XRD data does not correlate with the size of the grains, observed in the SEM image. Though, both XRD and SEM show nanoscale particle size. However, up-micro and the boundary of the particle are not proven so far by XRD [16].

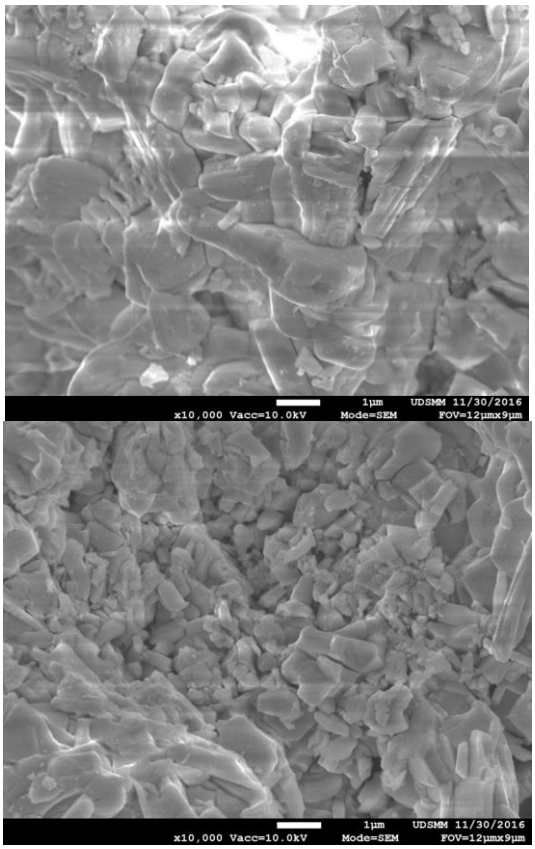


**Fig. 4.** SEM micrographs of $Bi_4Ti_3O_{12}$ ceramic.

## CONCLUSION

The mentioned method was already used for other oxide powders preparation, but we presented a new version. After hydrothermal treatment the powder was still amorphous and supplementary thermal treatment at 400 and finally at 600 °C was required. This process seems to afford a means of environmentally friendly and inexpensive aqueous synthesis.

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# ЗОЛ-ГЕЛ ХИДРОТЕРМАЛНО ПОЛУЧАВАНЕ НА $Bi_4Ti_3O_{12}$ КЕРАМИКА

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Постъпила на 28 ноември, 2017 г.; коригирана на 15 май, 2018 г.

(Резюме)

Представен е модифициран зол-гел метод за получаване на $Bi_4Ti_3O_{12}$ керамичен прах с последваща хидротермална обработка на получения гел. Бисмутов ацетат и титанов изопропоксид са използвани като източници на металите за получаване на прекурсорния гел, който успешно е превърнат в бисмут-титанов оксид чрез хидротермална обработка при 400 °C и 600 °C за 24 h. Продуктът е охарактеризиран посредством XRD, FTIR, SEM за определяне на неговите свойства и структурни характеристики.