

Synthesis by the polymeric precursor technique of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ and electrical properties dependence on the crystallite size

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Abstract

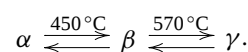
α - $\text{Bi}_2\text{VO}_{5.5}$ and γ - $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ specimens with different crystallite sizes have been synthesised by the citrate technique. The thermal evolution of the material was followed by powder X-ray diffraction (XRD) and differential thermal analysis (DTA). The synthesis of these materials is obtained via the formation of the intermediate BiVO_4 phase. Complete disappearance of BiVO_4 and completion of the reaction can only be achieved after the sample is annealed at 750 °C, leading to highly pure $\text{Bi}_2\text{VO}_{5.5}$ in the orthorhombic α -phase and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ in the tetragonal γ -phase. The effect of the crystallite size on the electrical conductivity of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ was investigated by impedance spectroscopy. The results indicate that the conductivity is significantly higher for materials with smaller crystallite size.

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1. Introduction

Aurivillius phases have the general formula $\text{Bi}_2\text{O}_2(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})$ and can be described as layered structures, consisting of perovskite blocks sandwiched between fluorite-like $(\text{Bi}_2\text{O}_2)^{2+}$ sheets. Amongst these materials, $\text{Bi}_2\text{VO}_{5.5}$ is a one-layer Aurivillius phase presenting two main phase transitions leading to three distinct phases α , β and γ [1]



Very high oxide ion conductivity is observed in its high temperature γ form ($\sigma > 10^{-1} \text{ S cm}^{-1}$ at $T > 500^\circ\text{C}$) that is characterised by the distortion of the V–O octahedra and oxygen vacancy disorder in the perovskite-like sheet $[\text{VO}_{3.5}\square_{0.5}]$ that disappears on cooling [1,2]. It is also the parent structure of the so-called BIMEVOX materials (BI stands for bismuth, ME for metal ion, V for vanadium, and OX for oxide), where the vanadium is partially replaced by other cations in order to stabilise the γ phase at lower temperature [3], but usually resulting in a degradation

of the ionic conductivity. The high electrical conductivity observed at low temperature in the BIMEVOX is attributed to the variable coordination of the vanadium ion in these materials, to the large concentration of vacancies, and to the polarizability of the Bi $6s^2$ lone pairs surrounding a conduction site in the vanadate layer [4]. Time dependence of the conductivity is usually observed with these materials, however, it has been shown that, provided the grain size is small enough, no thermal hysteresis nor time evolution of the electrical properties is observed [5].

The conventional solid-state method, that has been widely used to synthesise these materials, requires long reaction time at relatively high temperature, typically $T \sim 850^\circ\text{C}$ for 12 h [6]. Alternative synthesis routes to the traditional solid-state reaction, particularly those inducing a reduction of the size of the particles, might be able to improve the physical properties of these materials [4,5]. Synthesis of α - and γ - $\text{Bi}_2\text{VO}_{5.5}$ and other Bi-based materials have been reported by sol–gel [7], co-precipitation technique [8] and mechanically activated synthesis [9–11].

Here we present the studies by X-ray diffraction (XRD) and differential thermal analysis (DTA) of $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ prepared by the citrate (Pechini) method

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that has proved its efficiency to produce many materials with very fine particles [12]. A recent work on the BITIVOX synthesised by this method shows ionic conductivity values superior to the ones determined for BIMEVOX synthesised by traditional solid-state method [13]. Our main focus in the present work is the preparation by the citrate technique of both the parent structure $\text{Bi}_2\text{VO}_{5.5}$ and the highly conducting $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ (BICOVOX0.10) phase, and the influence of crystallite size on the electrical conductivity of the BICOVOX0.10.

2. Experimental

$\alpha\text{-Bi}_2\text{VO}_{5.5}$ and $\gamma\text{-Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ were prepared by the polymeric precursor technique, also known as the citrate or Pechini technique [14]. Stoichiometric amounts of Bi_2O_3 (Riedel-de Haen, 99.5%) and V_2O_5 , obtained from the calcination in air of finely divided vanadium metal (and additionally Co_2O_3 , in the case of the BICOVOX), were introduced in solutions of nitric acid. Each solution was mixed under heating, and a large amount of water was added until clear solutions were obtained. The resulting solutions were then added together and the mixture was heated at approximately 60°C for twenty minutes before the addition of citric acid. Ethylene glycol was added about twenty minutes later in the ratio citric acid:ethylene glycol 60:40 in mass. After some time of rigorous stirring under heating of the solution ($T \sim 150^\circ\text{C}$), a brownish resin was obtained; the resin was subsequently dried in air at 45°C overnight and calcinated for 1 h at 350 and 400°C for $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$, respectively, according to the results of the thermal analysis presented in the next section. The thermal behaviour of the resin was studied by differential thermal analysis and thermogravimetric analysis (TG) on a Netzsch STA 409 Simultaneous Thermal Analyser. TG and DTA measurements were performed up to 800°C at a heating rate of $10^\circ\text{C min}^{-1}$ under flowing synthetic air.

The powders were treated at several temperatures ranging from 250 to 750°C and characterised by powder X-ray diffraction with $\text{Cu-K}\alpha$ radiation carried out in the range $5\text{--}70^\circ$ in 2θ , with increments of 0.05° and counting time of 5 s per step on a Bruker-AXS D8 Advance diffractometer.

The electrical properties of BICOVOX samples were studied from 100 to 250°C by ac impedance spectroscopy using an HP 4192A impedance analyser in the $5\text{ Hz--}13\text{ MHz}$ frequency range. Gold contacts were deposited on the flat surfaces of the pellets by evaporation.

3. Results and discussions

The DTA curve obtained during heating of the resin presents a pronounced exothermic peak at approximately 275 and 310°C for $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$, respectively, that can be attributed to the combustion of the

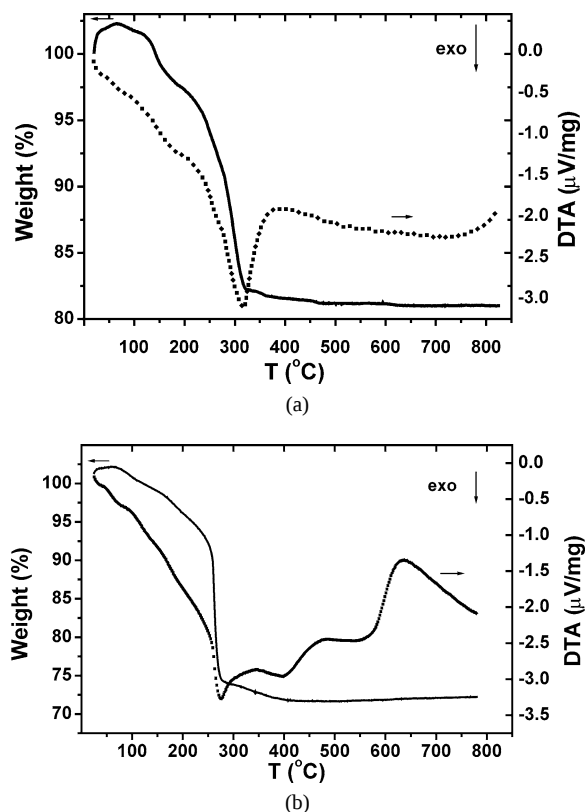
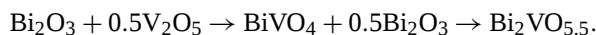


Fig. 1. Thermogravimetric and differential thermal analysis curves of precursor resins of (a) $\text{Bi}_2\text{VO}_{5.5}$ and (b) $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$.

organic substance, in agreement with the weight loss observed in the TG analysis (Fig. 1). These analyses showed that the decomposition of organic substances was complete by approximately 350°C for $\text{Bi}_2\text{VO}_{5.5}$ and 400°C for $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$. This shift from 350°C for $\text{Bi}_2\text{VO}_{5.5}$ to 400°C for $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ is probably related to the different thermal energy required for decomposition of specimens with different metal components.

X-ray pattern below that temperature is characteristic of an amorphous material (Fig. 2a). Powder X-ray diffraction of both products performed after 1 h calcination treatment at 350 and about 400°C for $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$, respectively, showed that a crystalline mixture of Bi_2O_3 and BiVO_4 is obtained at that stage (Fig. 2b and 2e). The $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ single phases are obtained after further annealing at 750°C for 2 h. According to these results, the synthesis process can be described with an intermediate BiVO_4 phase following the scheme as described by other authors for a different preparation method (mechanochemical synthesis) [15]



The BiVO_4 and $\text{Bi}_2\text{VO}_{5.5}/\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ phases co-exist until heat treatment at 750°C . Fig. 2 shows the evolution of the reaction after different thermal treatments of the powder. Only very small quantities of $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ are formed below 450°C , even after a

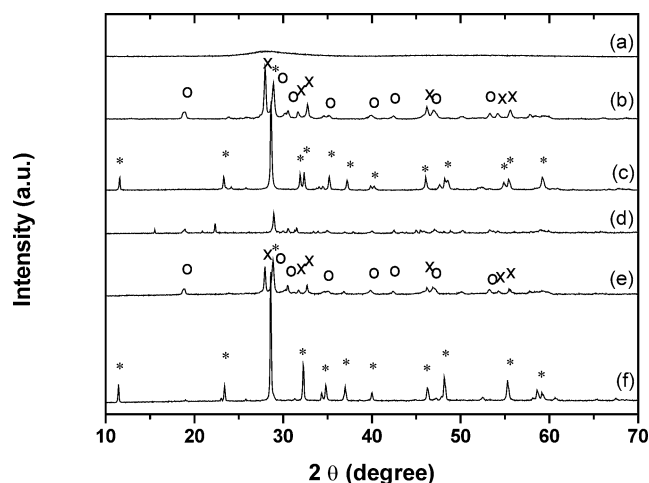


Fig. 2. X-ray diffraction patterns showing the $\text{Bi}_2\text{VO}_{5.5}$ and $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ phase formation after different heat treatment. (a) $\text{Bi}_2\text{VO}_{5.5}$ 250 °C/1 h, (b) $\text{Bi}_2\text{VO}_{5.5}$ 350 °C/16 h, (c) $\text{Bi}_2\text{VO}_{5.5}$ 750 °C/2 h, (d) $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ 250 °C/1 h, (e) $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ 400 °C/1 h and (f) $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ 750 °C/2 h. The main diffraction peaks of Bi_2O_3 (x), BiVO_4 (o) and $\text{Bi}_2\text{VO}_{5.5}/\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ (*) are shown.

long heat treatment (Fig. 2b and 2e). Materials heated at 650 °C for 16 h still present some trace of BiVO_4 , only eliminated after treatment at 750 °C (Fig. 2c and 2f).

Once single phase BICOVOX oxygen ionic conductor were prepared, we concentrated our work on the electrical properties of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ and their dependence on the crystallite size.

Two sintered samples of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ with different crystallite size were obtained after different heat treatment of the organic resin. After calcination of the resin of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ at 400 °C for both samples, and a further heat treatment at 650 °C for one of them, the powders were uniaxially pressed and the pellets sintered together with a powder bed of the same material at a temperature of 750 °C for 2 h. The apparent densities were determined by the weight and geometric dimensions of the pellet. The crystallite size of the sintered powders was estimated using Scherrer's equation $d_c = k\lambda/(\beta \cos \theta)$, where d_c is the crystallite size, k (~ 0.9) the shape factor, λ the X-ray wavelength, β the full width at half intensity of the diffraction line after correction of the instrumental broadening (by using a silicon standard) and θ the diffraction angle [16]. The values of the densities and crystallite size are shown in Table 1. The relative densities were calculated using the theoretical density value already reported [17].

Table 1
Calculated and relative densities* (in %) of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ pellets and crystallite size after sintering of powders calcinated at 400 and 650 °C

Density (g cm^{-3})	d_c (nm)
6.86 (88%)	58
6.45 (83%)	154

* Theoretical density = 7.77 g cm^{-3} .

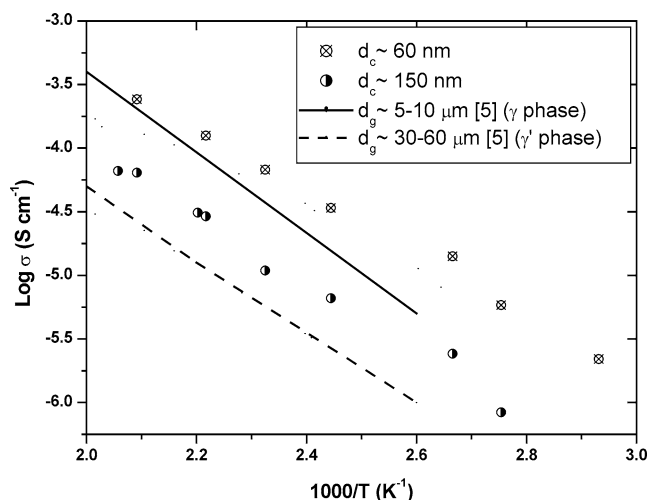


Fig. 3. Arrhenius plot of the electrical conductivity of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ with different crystallite size (d_c) and grain size (d_g) according to Ref. [5].

The impedance diagrams obtained for these samples can be separated into two semicircles [18]. These semicircles can be attributed to the bulk and grain boundary contributions to the resistivity at high and low frequency, respectively.

Because gold contacts do not endure high temperature, due to the method of deposition, conductivity measurements had to be limited to 250 °C.

The Arrhenius-type graphs of the total conductivity of these compounds have been plotted and are shown in Fig. 3. The value of the activation energy was found to be $\sim 0.50 \text{ eV}$. As can be seen on the Arrhenius plots, the obtained results depend on the crystallite size of the samples. Higher conductivity is observed with the samples with $d_c \sim 60 \text{ nm}$ than with the sample with $d_c \sim 150 \text{ nm}$. Similar effects with pellets of BICOVOX0.10 with different grain size (d_g) have already been observed [5], which confirms the stabilisation of the highly conducting phase for samples with small crystallite/grain size.

In Table 2, the conductivity of the samples here reported are compared with the conductivity of the same material prepared by solid state reaction [19]. The highest conductivity is observed for BICOVOX0.10 with crystallite size of $\sim 60 \text{ nm}$, obtained in the present study. Depending on the synthesis route, the observed activation energies vary, this can be explained by the different mobility of the charge carriers due to different microstructures.

Although, the sample with crystallite size of $\sim 60 \text{ nm}$ has a higher density value, this should not affect so significantly the conductivity. In their work on yttria-stabilised zirconia, Santos et al. established that the bulk conductivity is affected by the porosity according to the following equation [20]:

$$\sigma_{\text{bulk}} = \sigma_{\text{bulk}}^0 (1 - P)^{2.74},$$

where σ_{bulk} is the conductivity measured for the sample of porosity P and σ_{bulk}^0 that of a fully dense material.

If we consider that the same equation applies to our material, then the bulk conductivity of the denser sample

Table 2

Values of the activation energies E_a , E_a (b) and E_a (gb) related to the total, bulk and grain boundary contributions, respectively, and total conductivity σ around $T = 200^\circ\text{C}$

Material	E_a (eV)	E_a (b) (eV)	E_a (gb) (eV)	σ (S cm^{-1})	T ($^\circ\text{C}$)	Ref.
$\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ ($d_c \sim 60$ nm)	0.47(2)	0.47(2)	0.43(2)	2.42×10^{-4}	205	This work
$\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ ($d_c \sim 150$ nm)	0.54(3)	0.52(3)	0.63(3)	6.43×10^{-5}	201	This work
$\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$	0.62	0.61	0.65	1.40×10^{-4}	227	[19]

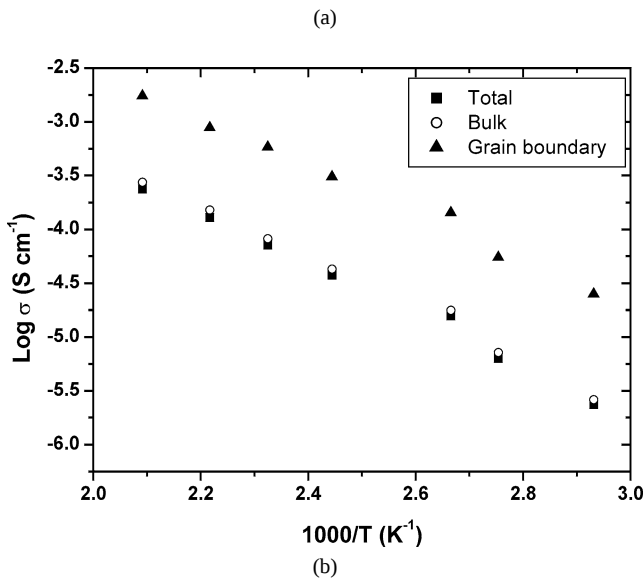
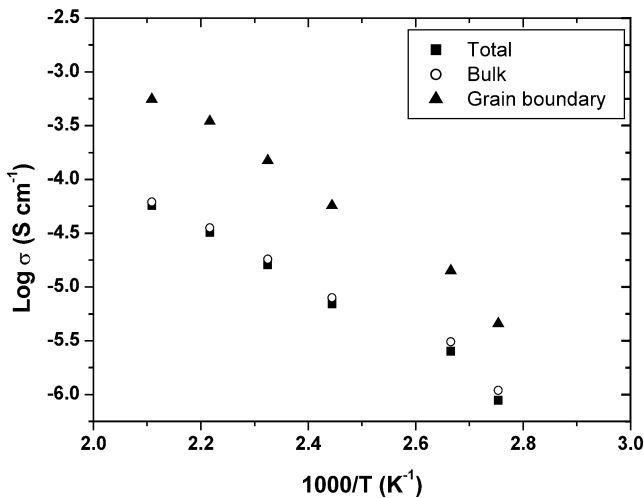


Fig. 4. Arrhenius plot of the grain boundary, bulk and total electrical conductivities of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ with $d_c \sim 150$ nm (a) and $d_c \sim 60$ nm (b).

($d_c \sim 60$ nm, 88% of theoretical density) should be 1.16 times higher than the more porous one ($d_c \sim 150$ nm, 83% of theoretical density), which is much lower than the observed increase in bulk conductivity (Fig. 4).

Such a significant increase of conductivity between the samples of different d_c cannot be explained by the small difference in measured density.

Another representation of the evolution of the resistivity as a function of temperature can be visualised using the blocking factor α_{gb} , which represents the fraction of charge

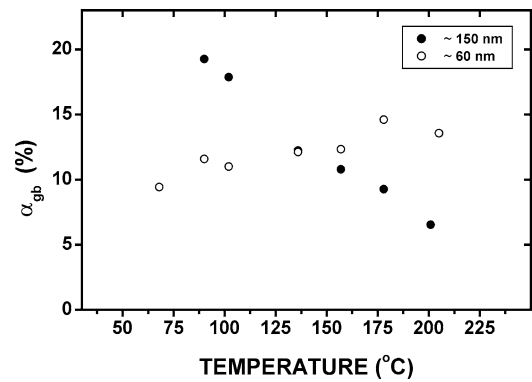


Fig. 5. Variation of the blocking factor of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ with different crystallite size (d_c) as a function of the temperature.

carriers being blocked at the grain boundaries [21]. The blocking factor is calculated using the following equation:

$$\alpha_{gb} = R_{gb}/R_t,$$

where R_{gb} is the resistance due to grain boundaries and R_t is the total resistance [21].

One should expect a lower blocking factor for larger crystallite size, as the relative resistance due to grain boundary is lower when the grains are larger. This is observed in yttria-stabilised zirconia, for example, [20]. However, in our case the blocking factor of the sample with larger crystallite size is higher at low temperature and lower at higher temperature than in the samples with smaller crystallite size. The temperature dependence of the blocking factor for $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ specimens with different crystallite sizes is shown in Fig. 5.

A decrease of the blocking factor with increasing temperature is observed for the specimen with $d_c \sim 150$ nm. Such an evolution was not observed for the smaller crystallite size sample in the investigated temperature range. The blocking factor due to grain boundaries decreases for the large crystallite sample, while it remains constant for the small crystallites sample. A similar effect was reported for BICUVOX and BICOVOX with different grains sizes [19]. In this work, the authors analyse that their BICUVOX sample, with relatively larger grain size, presents higher conduction anisotropy than the BICOVOX, with smaller grain size, due to anisotropic grain growth. In our study, we observed that the BICOVOX sample with larger crystallite size behaves similarly to the BICUVOX presenting anisotropic grain growth.

4. Conclusions

BIMEVOX materials of high purity were successfully prepared by the citrate technique. The formation of the final product proceeds through an intermediate BiVO_4 phase eliminated by heating at 750°C .

Compounds of $\text{Bi}_2\text{Co}_{0.1}\text{V}_{0.9}\text{O}_{5.35}$ of different crystallite sizes have been produced. The conductivity of the sample with crystallite size of ~ 150 nm is in the same range than that of similar material prepared by traditional solid state reaction, while a significant increase of the conductivity is observed with smaller crystallite size ($\sigma = 2.42 \times 10^{-4} \text{ S cm}^{-1}$ at 205°C for crystallite size of ~ 60 nm).

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