

1-1-2006

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BAYKAL, ABDULHADİ and EVREN, AYTEN (2006) "Hydrothermal and Microwave-Assisted Synthesis of Boroarsenate, BAsO<sub>4</sub>," *Turkish Journal of Chemistry*. Vol. 30: No. 6, Article 8. Available at: <https://journals.tubitak.gov.tr/chem/vol30/iss6/8>

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# Hydrothermal and Microwave-Assisted Synthesis of Boroarsenate, $\text{BAsO}_4$

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Received 21.04.2006

$\text{BAsO}_4$  was previously synthesized by solid-state reactions at 800 °C and was characterized by X-ray powder diffraction. Now, we succeeded in preparing  $\text{BAsO}_4$  from  $\text{H}_3\text{BO}_3$  and  $\text{As}_2\text{O}_5$  using hydrothermal synthesis by heating at 160 °C for 3 days (a single-phase product) and using microwave-assisted synthesis, which takes only 5 min to transform a solid mixture of  $\text{As}_2\text{O}_5$  and  $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  into the crystalline titled compound (a single-phase product). The crystallinity of the products is higher than that of the solid-state synthesized product given in the literature. Its X-ray powder diffraction patterns, and both Raman and IR spectra were in good agreement with the literature.

**Key Words:** Boron arsenate,  $\text{BAsO}_4$ , microwave synthesis, hydrothermal synthesis and X-ray diffraction.

## Introduction

Borophosphates with open-framework structures analogous to zeolites are of great interest because of their potential use as catalyst ion-exchangers, molecular sieves, etc.<sup>1–3</sup> In contrast, the area of boroarsenate chemistry has been poorly explored, with very few known examples in the current literature. The minerals teruggite  $[\text{Ca}_4\text{Mg}(\text{B}_6(\text{OH})_6\text{O}_8(\text{AsO}_3)_2(\text{H}_2\text{O})_{14})]$  and cahnite  $[\text{Ca}_2\text{BAsO}_4(\text{OH})_4]$ , which contain discrete  $\text{B}(\text{O},\text{OH})_4$  and  $\text{As}(\text{OH})_4$  tetrahedra, are known, as are a few dense boroarsenates prepared at high temperature, including  $\text{Ba}(\text{BAsO}_5)$ ,  $\text{Pb}(\text{BAsO}_5)$ , and  $\text{Pb}_6\text{AsO}_4(\text{B}(\text{AsO}_4))$ . Thus, the investigation of these arsenate species provides an opportunity to develop completely new framework types, quite distinct from borophosphates, which can coordinate with anionic species through the proton of the OH unit, or hydrogen bond within channels.<sup>4</sup>

In recent years, much progress has been made in the synthesis of materials by hydrothermal and microwave methods. Conventional techniques, such as solid-state reactions at high temperatures, or photochemical, catalytic, ultrasonic, and high-pressure reactions, are used to stimulate chemical reactions that proceed slowly under ambient conditions.<sup>5</sup> On the other hand, the use of controlled microwave energy for ceramic processing and drying, and for melting silica, alumina, and aluminosilicate gels has been reported.<sup>6</sup>

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The basic idea for a microwave-assisted preparation of borophosphates and boroarsenates is consistent with the observation of the high microwave susceptibilities of those phosphate, arsenate, and borate hydrates.<sup>7–10</sup>

During the last few years, the chemical solution routes have successively emerged as effective, convenient, energy efficient, and material efficient synthetic techniques for material preparation. Among them, the hydrothermal route is one of the most used, due to its economy and high degree of compositional control. Hydrothermal synthesis requires neither an extremely high processing temperature nor sophisticated processing. For example, ferrites can be prepared via the hydrothermal method at a temperature of about 150 °C, whereas the solid-state method requires a temperature of 800 °C.<sup>11</sup>

BAsO<sub>4</sub> was first prepared from B<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub> by solid-state synthesis at high temperature, according to Schulze.<sup>12</sup> The crystal structure contains BO<sub>4</sub> and AsO<sub>4</sub> tetrahedra. BAsO<sub>4</sub> is a copolymer of 2 soluble and low-melting oxides: boric oxide and arsenic oxide. It is insoluble in water, chemically inert, and has a high softening point. It is a four-connective crystalline polymer whose structure (Figure1) is similar to that of silica.<sup>13</sup>

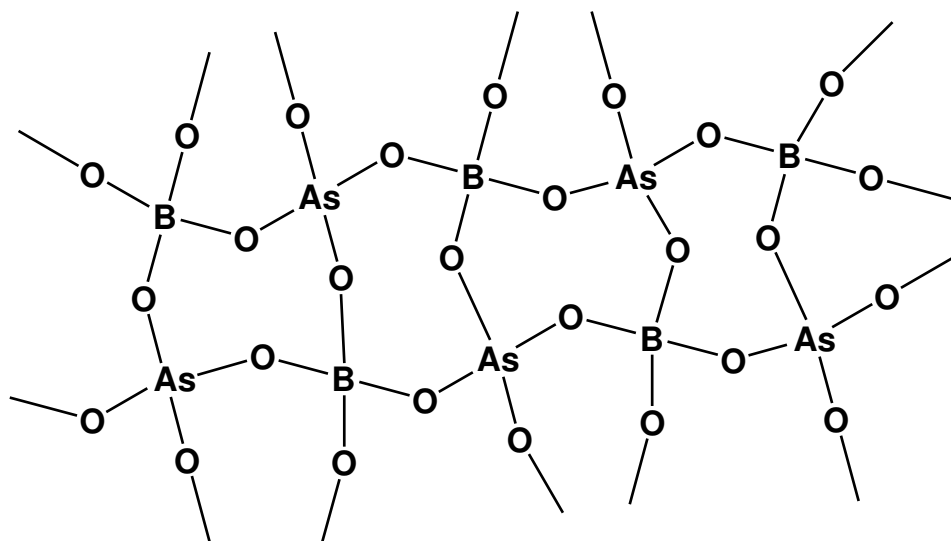


Figure 1. Boron arsenate projected on a lane.

BAsO<sub>4</sub> and BPO<sub>4</sub> are isostructural compounds. Reports in the literature concerning BPO<sub>4</sub> and BAsO<sub>4</sub> are extremely limited, and both materials crystallize in a cristobalite-related structure under ambient conditions.<sup>14,15</sup> In this work, we developed previously unreported simple and fast microwave-assisted and hydrothermal methods for the synthesis of BAsO<sub>4</sub>.

## Experimental

### Substances

As<sub>2</sub>O<sub>3</sub> and As<sub>2</sub>O<sub>5</sub> (synthesized in our laboratory), H<sub>3</sub>BO<sub>3</sub>, (NH<sub>4</sub>)<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·4H<sub>2</sub>O, and B<sub>2</sub>O<sub>3</sub>.

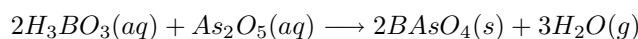
## Instruments

X-ray powder diffraction data of the products were measured on a Rigaku diffractometer (Cu  $K_{\alpha}$ , 40 kV, 20 mA,  $\lambda = 1.54056 \text{ \AA}$ ) with D/max RINT-2200. The infrared transmittance spectra were measured at room temperature in a KBr disc using a Shimadzu FTIR infrared spectrometer in the frequency range of 400-4000  $\text{cm}^{-1}$ . The room temperature Raman scattering (RS) spectra of the compounds were obtained with a Bruker RFS 100/S spectrometer.

Microwave reactions were carried out in an Arçelik MD 58 I consumer model microwave oven (2.450 GHz, 1000 W).

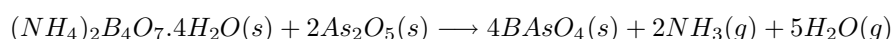
### a) Hydrothermal Synthesis of $\text{BAsO}_4$

The hydrothermal synthesis of  $\text{BAsO}_4$  was carried out by starting with a 5.2-g mixture of  $\text{H}_3\text{BO}_3$  (3.2 g) and  $\text{As}_2\text{O}_5$  (2 g) (prepared by the reaction of arsenic(III) oxide with nitric acid, followed by the dehydration of the arsenic acid thus formed in a closed system) in a 6:1 molar ratio (boron flux method). The reactants were mixed in 25 mL of distilled water and stirred until the components completely dissolved. The clear solution was heated without boiling and concentrated to 15 mL, and was then transferred to a Teflon autoclave (65% filled) and heated to 160 °C for 3 days. The crystalline products were filtered off in vacuo, washed with distilled water, and dried at 60 °C.



### b) Microwave-Assisted Synthesis of $\text{BAsO}_4$

For microwave-assisted synthesis of  $\text{BAsO}_4$ , a dry and ground solid-state 2.74-g mixture of  $(\text{NH}_4)_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$  (1 g) and  $\text{As}_2\text{O}_5$  (1.74 g) with a molar ratio of 1:2 was placed in a Teflon beaker and treated in a conventional kitchen microwave oven (2.450 GHz; max 1000 W) for 5 min. The mixture partially melted after exposure to microwave radiation and copious bubbling of the materials was observed. After 5 min, the irradiation was terminated and the sample was allowed to cool inside the oven (80 °C for 2 h). The proposed reaction for the microwave-assisted synthesis of  $\text{BAsO}_4$  is as follows:



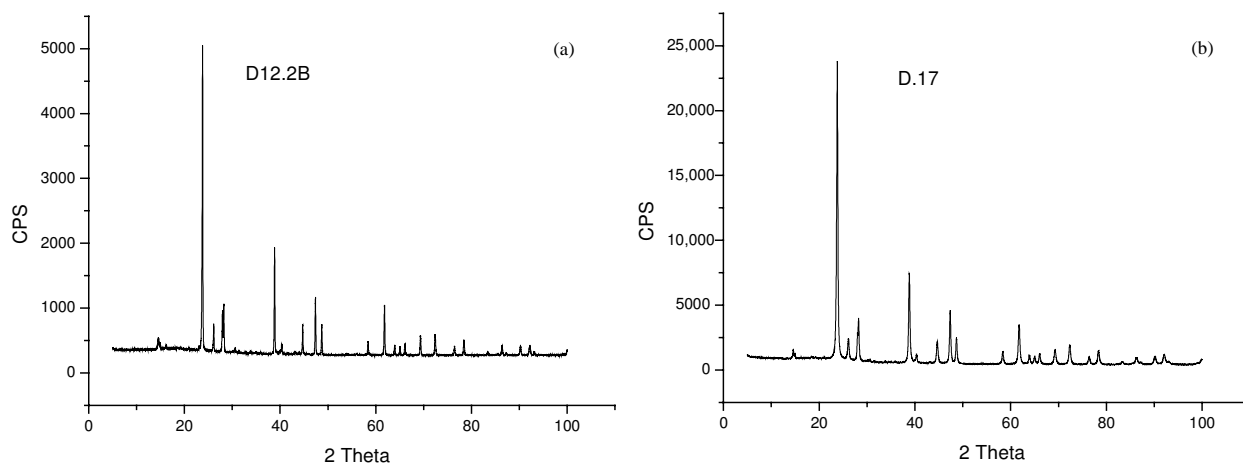
## Results and Discussion

Percent conversion of reactants in both the hydrothermal and microwave-assisted methods is complete (100%). The crystal structure of  $\text{BAsO}_4$  obtained in all reactions is tetragonal. The reported unit cell parameters are  $a = 4.458$  and  $c = 6.796$  space group I(-4) (No:82), which are in good agreement with our unit cell parameters.<sup>14,15</sup>

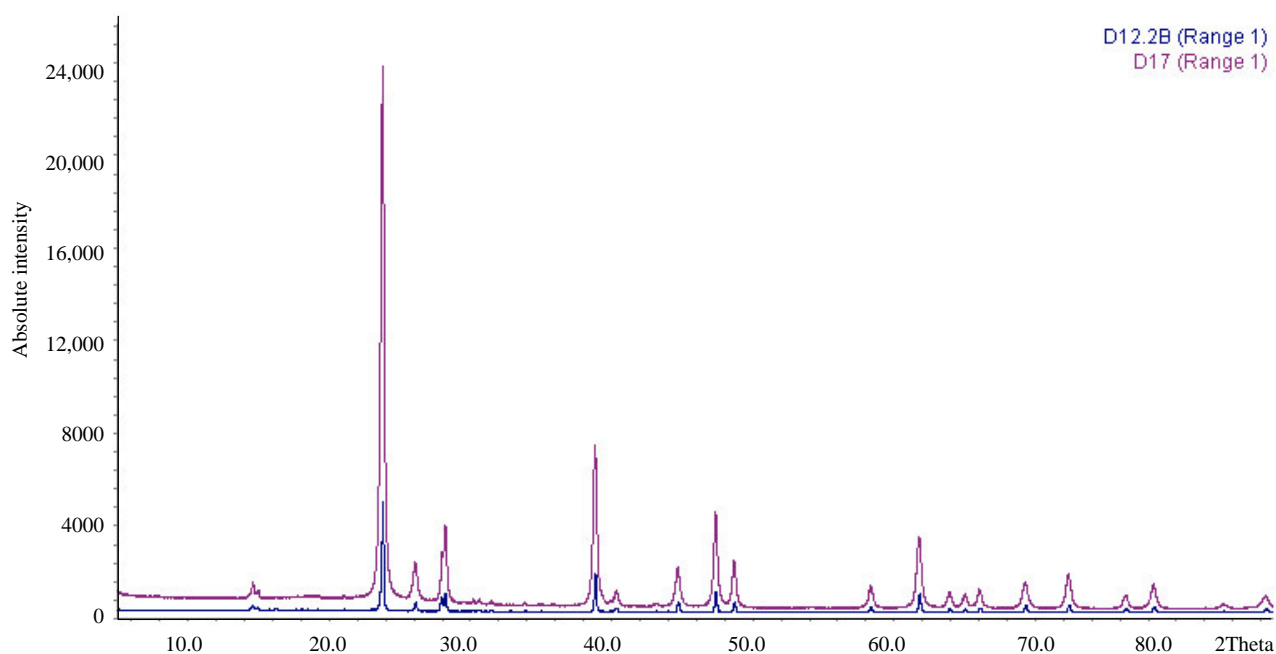
The first step of the microwave-assisted reaction (4 min) is the loss of water molecules from the components. Then, the temperature of the mixture in microwave-assisted synthesis rises very rapidly and the mixture continues to glow during the reaction. Flashes were continuously seen emanating from the bulk of the reaction mixture. Unfortunately, with our microwave system, it was impossible to measure the temperature accurately during the glowing, but it was assumed to be between 870 and 1100 K, according to

Vaidhyanathan et al.<sup>9</sup> They estimated these temperatures by conducting some experiments with nitrides in open atmosphere.

The XRD powder patterns of  $\text{BaSO}_4$  produced by the hydrothermal (D12.2B) and microwave-assisted (D-17) methods are shown in Figure 2, and the comparison of XRD powder patterns of experiment D-12.2B (hydrothermal) and D-17 (microwave-assisted) appear in Figure 3.



**Figure 2.** X-ray diffraction powder pattern of  $\text{BaSO}_4$  produced by the hydrothermal method (D12.2B) and microwave-assisted method (D-17).



**Figure 3.** Comparison of XRD powder patterns of experiment D-12.2B (hydrothermal) and D-17 (microwave-assisted).

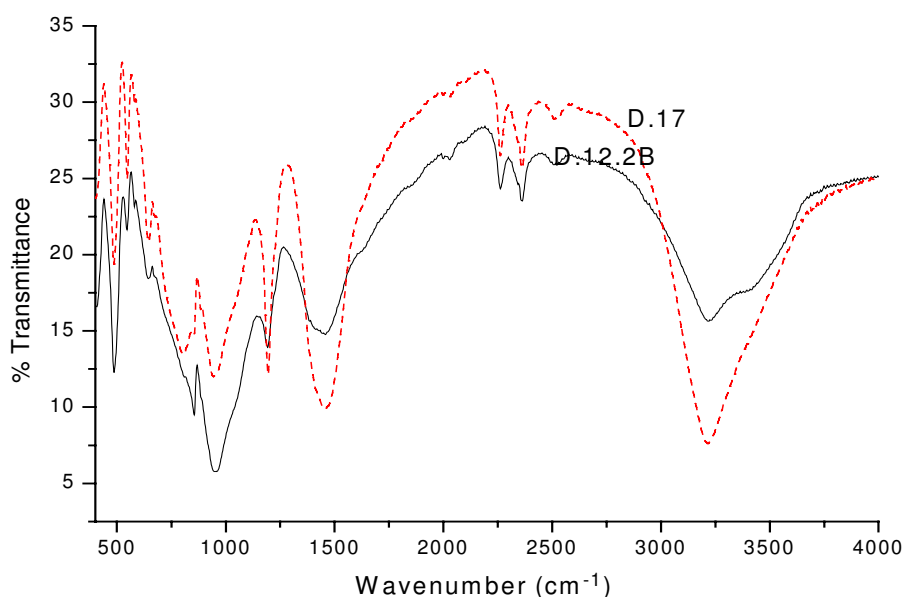
## FTIR Studies of $\text{BAsO}_4$

Although vibrational spectroscopy has been widely used in examining  $\text{AsO}_4^{3-}$  coordination chemistry, insufficient knowledge of the correlation of the  $\text{AsO}_4^{3-}$  molecular structure and its vibrational spectra impeded its complete spectral interpretation.<sup>16,17</sup>

There is an assignment problem for the arsenates since both symmetric and antisymmetric modes have very similar frequencies. Additionally, since isotopic frequencies are not available (there is only one stable isotope of arsenic), the discrimination between symmetric and antisymmetric modes is impossible and the group of bands in the  $750\text{--}900\text{ cm}^{-1}$  region is simply assigned to the stretching motions ( $\nu_1$  and  $\nu_3$ ) without any further specification.

Boron, tetrahedrally coordinated to oxygen, displays stretching modes in the region of  $1100\text{--}850\text{ cm}^{-1}$  and the most probable assignment is that the bands, due to the antisymmetric stretching mode, are centered at about  $1050\text{ cm}^{-1}$ . The symmetric stretching frequency is located in the  $850\text{--}900\text{ cm}^{-1}$  region.<sup>18</sup>

The IR spectrum of  $\text{BAsO}_4$  (Figure 4) was found to be in good agreement with the bands of  $\text{AsO}_4$ , B-O-As, and  $\text{BO}_4$  groups of  $\text{BAsO}_4$  given in the literature.<sup>19</sup> The band at  $1211\text{ cm}^{-1}$  is characteristic of the tetrahedral  $\text{BO}_4$  group ( $\nu_{as}$ ) and the symmetric mode is in the shoulder of the band at  $948\text{ cm}^{-1}$ . The band at  $948\text{ cm}^{-1}$  is assigned to B-O-As asymmetric and symmetric vibrations, and the characteristic bands of the tetrahedral  $\text{AsO}_4$  group ( $\nu_s$ ,  $\nu_{as}$ ) are at  $800\text{ cm}^{-1}$ . Other bands at  $1640$ ,  $3450$ ,  $3215$ , and  $3332\text{ cm}^{-1}$  are the OH vibrations of liquid  $\text{H}_2\text{O}$  and the H-bond between  $\text{H}_2\text{O}$  and  $\text{AsO}_4^{3-}$ .



**Figure 4.** FTIR spectra of  $\text{BAsO}_4$  produced by the hydrothermal method (D-12.2B) and microwave-assisted method (D-17).

## Raman Studies of $\text{BAsO}_4$

Raman peaks are observed in the  $800\text{--}900\text{ cm}^{-1}$  region for the arsenates. One of these peaks is of much greater intensity than the others and is assigned to an essentially symmetric stretching mode ( $\nu_1$  of the free

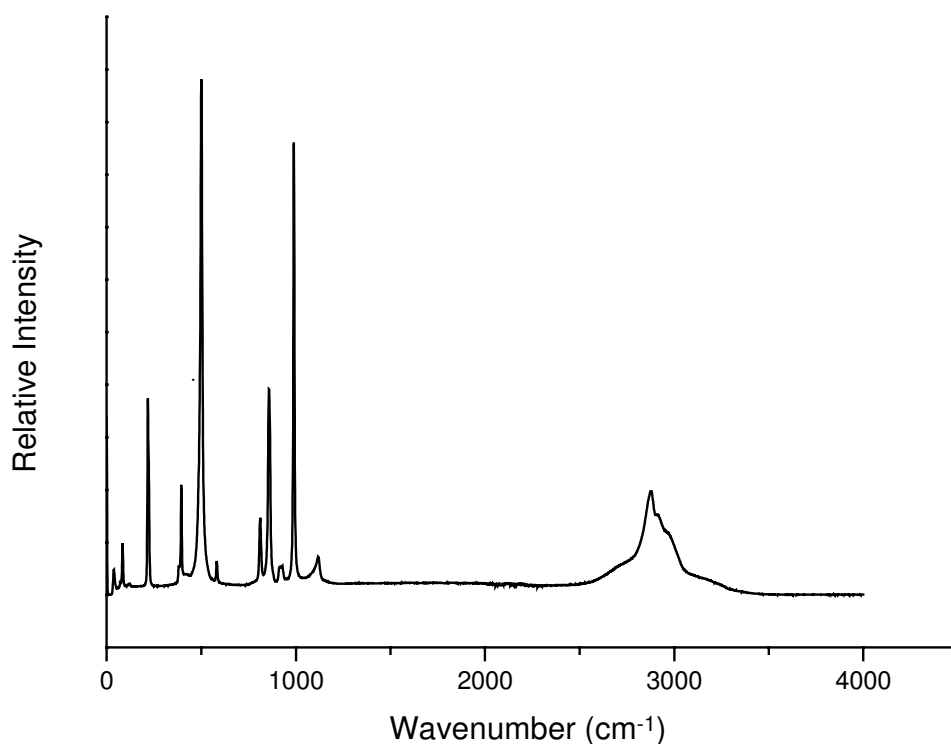
ion).

For the arsenates, the assignment must rely on intensity considerations alone, since symmetric and antisymmetric modes have similar frequencies.

The symmetric vibrations of the arsenate anion ( $\nu_1$ ) are observed at  $810\text{ cm}^{-1}$  and coincide with the position of the asymmetric stretching mode ( $\nu_3$ ).<sup>20–23</sup> The symmetric bending mode ( $\nu_2$ ) is observed at  $342\text{ cm}^{-1}$  and the out-of-plane bending mode ( $\nu_4$ ) is observed at  $398\text{ cm}^{-1}$ .<sup>24</sup>

The Raman spectrum of the  $\text{BAsO}_4$  (Figure 5) was in good agreement with the bands of  $\text{AsO}_4$ , B-O-As, and  $\text{BO}_4$  groups of  $\text{BAsO}_4$  given in the literature. There are 3 parts of the spectra. The first part consists of the main bands: one asymmetric stretching band of  $\text{BO}_4$  is seen at about  $1125\text{ cm}^{-1}$  and one symmetric stretching band of  $\text{BO}_4$  is seen at about  $1000\text{ cm}^{-1}$ . After the  $\text{BO}_4$  group, the B-O-As group is seen, and lastly there are 2 bands that are assigned to asymmetric and symmetric stretching bands of  $\text{AsO}_4$ . The second part is assigned to the ring deformation bands and the last part is assigned to the lattice modes. The bands around  $3000\text{ cm}^{-1}$  belong to the OH vibrations of liquid water and the H-band between  $\text{H}_2\text{O}$  and  $\text{AsO}_4$ .

The hydrothermally synthesized  $\text{BAsO}_4$  Raman spectra are given in Figure 5.



**Figure 5.** Raman spectra of hydrothermally synthesized  $\text{BAsO}_4$  (D12.2B).

## Conclusion

In this study, boron arsenate,  $\text{BAsO}_4$ , was successfully synthesized through solid-state, hydrothermal, and microwave-assisted reactions. Compared to traditional methods, microwave synthesis has several advantages, including a considerably reduced processing time and energy savings. This method and the hydrothermal method appear to be good alternatives for the synthesis of  $\text{BAsO}_4$ . The XRD powder pattern, FTIR, and

Raman spectra are in good agreement with published data.  $\text{BaSO}_4$  was synthesized by hydrothermal and microwave-assisted methods for the first time in this study.

## Acknowledgment

The authors are grateful to Prof. Dr. Mehmet SOMER (Koç University) for the Raman measurements and to the Fatih University Research Project Foundation (Contract no: P50020203) for its financial support of this study.

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