

## Location of 6-azonia-spiro-[5,5]-undecane molecules in ZSM-12 using X-ray synchrotron powder diffraction data

Annalisa Martucci<sup>\*[a]</sup>, Lara Gigli<sup>[b]</sup>, Jasper Rikkert Plaisier<sup>[b]</sup>

[a] Department of Physics and Earth Sciences, University of Ferrara Via Saragat 1, I-44121, Ferrara, Italy E-mail: mrs@unife.it

[b] Elettra-Sincrotrone Trieste S.C.p.A., Materials Characterisation by X-ray diffraction (MCX) beamline, Strada Statale 14 - km 163,5 in AREA Science Park, Basovizza, Trieste, Italy

\*Corresponding authors: Annalisa Martucci

### Abstract

High-silica ZSM-12 (MTW topology), synthesized with 6-azonia-spiro-[5,5]-undecane as structure directing agent (SDA), was carefully characterized by using X-ray synchrotron powder diffraction. The structure refinement led to a monoclinic unit cell (space group  $Cc$ ,  $Z=4$ ,  $a = 25.0814(13)$  Å,  $b = 15.0987(8)$  Å,  $c = 24.4419(17)$  Å,  $\beta = 107.844(6)$ ,  $V = 8810.8(8)$  Å<sup>3</sup>) with a three times enlargement of the unit cell along the  $b$  axis with respect to the calcined starting ZSM-12 (space group  $C2/c$ ,  $Z=1$ ,  $a = 24.8633(3)$  Å,  $b = 5.01238(7)$  Å,  $c = 24.3275(7)$  Å,  $\beta = 107.7215(6)^\circ$ ). The SDAs conformation and position in the framework structure did not maintain the twofold axes coinciding with the crystallographic twofold axis thus changing the space group symmetry from  $C2/c$  to  $Cc$ . The structure refinement gave an extraframework content 6.13 SDA molecules per unit cell (corresponding to ~9.0 wt%) in good agreement with the weight loss given by the thermogravimetric analysis. The refined bond distances revealed the occurrence of non-bonding interactions of both azonia molecules with the MTW pore wall. AZO-1 and AZO-2 molecules are H-bonded between them thus forming clusters aligned along the  $b$  axis. This information is crucial to tailor the physicochemical properties of zeolites as well as to address their hydrophobicity, pore dimensions and cavities thus optimizing the selectivity of zeolite catalysts.

**Keywords:** 6-azonia-spiro-[5,5]-undecane, ZSM-12, X-ray synchrotron powder diffraction data, SDA conformation, Rietveld refinement.

## 1. Introduction

Zeolites and related zeotypes are crystalline molecular sieves consisting of three-dimensional networks of corner-sharing  $[TO_4]$  tetrahedra (T = Si, Al, P, B, Ti, Sn etc.) with regular pores and cages with free dimensions in the range 3–20 Å. The possibility to synthesize zeolites with different pore topologies and chemical compositions promotes advanced applications in catalysis, gas adsorption and separation, ion exchange, electronics, environmental protection as well as in medicine, nanotechnology, photonics, microelectronics, and bioengineering [1-5]. Some of the zeolite properties can be tuned during their synthesis by controlling crystal size and/or chemical composition, pore dimensions and their connectivity through the use of organic or inorganic structure-directing agents (SDAs) [6-7]. The detection of SDAs able to tailor the physicochemical properties of zeolites has attracted increasing attention because it combines the advantages to address their hydrophobicity, pore dimensions and cavities thus optimizing the selectivity of zeolite catalysts [8-10]. Much effort has been put in order to a priori predict the energetically stable SDA arrangement and conformation and minimize van der Waals and electrostatic SDA-framework energy of interactions by using computational modeling or the “ab initio” design [11-19]. Computer modelling approaches have been developed to predict the location and conformation adopted by the template molecules during the zeolite synthesis as well as to calculate molecular structures, energetics, dynamics, and reactivities within the host [20-31].

Less frequently, diffraction techniques are used as a tool to obtain structural information concerning long-range ordering but, as far as location and distribution of SDAs are concerned, uncertainties or ambiguities often persist due to the occurrence of very disordered local bonding geometries.

Azonia-spiro-alkanes (ASK) I, II, III (5-azonia-spiro-[4,5]-decane, 6-azonia-spiro-[5,5]-undecane, 6-azonia-spiro-[5,6]-dodecane, respectively) form an interesting class of organic SDAs used for the first time in SSZ-19 zeolite synthesis back to the middle of the 1980s using 5-azonia-spiro-[4,4]-nonane [32]. The presence of the two cyclic moieties offers the possibility to synthesize a wide variety of structures such as MOR, EUO, MTW, as well as intergrowths of NON, EUO and NES, siliceous zeolites such as BEC and more recently germanosilicates such as IM-12 and IM-9 [33-43].

However, along exploratory syntheses, new microporous phases, named ERS-10 [44-46] and ERS-18 (EEI) [47-48], were identified using 6-azonia-spiro-[5,5]-undecane (ASK II) as structure directing agent.

In this paper, we report on the structure determination of high-silica ZSM-12 (MTW topology) synthesized with 6-azonia-spiro-[5,5]-undecane template using X-ray synchrotron powder diffraction data, with the aim to discern its conformation and position in the framework structure. The interactions between the SDAs and the ZSM-12 framework are evaluated from experimental data

with reasonable approximation and then optimized using the geometry optimization tool in order to minimize the energy of the crystal structure as well as provide reasonable bond lengths and angles and calculate the position of the H atoms.

## 2. Experimental

High-silica ZSM-12 used in this work was synthesized with ASK II (labelled ZSM-12-ASK-II from now) starting from a mixture composed by NaOH, the aluminum source and the SDA then dissolved in demineralized water and heated at 353 K. This sample corresponds to MTW II-7 synthesized by Millini et al. [44], using a reaction mixture with  $\text{SiO}_2/\text{Al}_2\text{O}_3 = 200$ ,  $\text{R}/\text{SiO}_2=0.25$  (molar ratios in the reaction mixture),  $\text{Na}^+/\text{SiO}_2=0.05$  (molar ratios in the reaction mixture),  $\text{H}_2\text{O}/\text{SiO}_2=45$  (molar ratios in the reaction mixture),  $\text{pH}=13.62$  (initial pH value of the reaction mixture) and  $T=443$  K.  $^{13}\text{C}$  MAS NMR spectra collected for the MTW pore systems give  $\text{C-}\alpha=60(900)$ ,  $\text{C-}\beta=21(1000)$ ,  $\text{C-}\gamma=21(1000)$  [44].

The powders were then heated in a furnace for three hours at about 600 °C in order to obtain the calcined form (labelled ZSM-12-C to follow).

Thermal analyses (TG and DTA) were performed on a STA 409 PC LUXXX® - Netzsch on both ZSM-12-ASK-II and ZSM-12-C samples. The measurements were carried out in air flow up to 900 °C with a heating rate of 10°C/min. The powder diffraction patterns of the two samples were collected at the MCX beamline [49-50] of Elettra - Sincrotrone Trieste, (Italy) in transmission mode, at room temperature (25°C) with a monochromatic wavelength of 0.827 Å (15 keV) and 1.0 × 0.3 mm<sup>2</sup> spot size. They were then loaded and packed in a 0.5 mm boron-glass capillary, mounted on a standard goniometric head and spun during data collection. The structure solution by the direct space approach was performed using the EXPO2014 program [51]. The obtained unit cell parameters were refined using whole powder pattern fitting (LeBail method) [52] (Table 1). All data processing was carried out by full profile Rietveld analysis using the GSAS package [53] with the EXPGUI interface [54]. The profile was modelled by a pseudo-Voigt function (which uses an accurate description of the reflection asymmetry due to axial divergence described by Finger et al. [55] as an implementation of the peak shape function described by Van Laar & Yelon [56]). The background was first edited manually and further empirically fitted using a Chebyshev polynomial with 24 polynomial coefficients. The scale factor, 2θ-zero shift, and unit-cell parameters were accurately refined. The thermal displacement parameters were constrained in the following way: the same value for all the tetrahedral atoms and a second value for all the framework oxygen atoms. The extra-framework sites were located by difference Fourier maps and H-atoms were not considered within the structure

refinement due to their low scattering factors. Soft restraints were applied on the tetrahedral cations and coordinated framework oxygen atom distances during all stages of refinement, and their weight was progressively reduced in the last cycles. Due to the inseparability of structural analysis from the results, the former are better discussed in Results and Discussion. Final crystal and refinement data are reported in Table 1. The detailed structural data of the final structure are (mol and cif files) reported as supplementary information (Table 1SI, Table 2SI).

## Results and discussion

A close look at the PXRD pattern of ZSM-12-ASK-II highlights the presence of several diffraction peaks (at 10.17, 14.22, 19.38, 20.88, 21.30, 22.42, 26.26, 31.12 and 34.98 ° 2 $\theta$ , respectively) not detected in the same calcined sample (Figure 1). The difference in the Bragg's peak intensities are significant thus highlighting that the SDA package affects both the structural and atomic parameters. This assumption was confirmed by their disappearance in the powder pattern after ZSM-12 calcination thus verifying the link between their occurrence and the presence of the template molecules. In accordance with Rodeghero et al. [57] all the major reflections could be indexed with the well-known space group  $C2/c$  ( $a = 24.8633(3)$  Å,  $b = 5.01238(7)$  Å,  $c = 24.3275(7)$  Å,  $\beta = 107.7215(6)^\circ$ , cell formula units  $Z=1$  first reported by Fyfe et al. [58] (Table 1).

To index the ZSM-12-ASK-II pattern, the program EXPO2014 [51] was used, without the imposition of any symmetry restraints. The solution led to a meaningful model which perfectly fits the unindexed peaks using a larger monoclinic unit cell (space group  $Cc$ ,  $Z=4$ ) with a three times enlargement of the unit cell along the  $b$  axis with respect to that the calcined ZSM-12-C. A similar case, where the pure-silica ZSM-12-unit cell showed the  $b$  axis tripled, has been reported by Kasunic et al [59] for ZSM-12 synthesized in the presence of tetraethylammonium (TEA) cations ( $a = 25.2177(9)$  Å,  $b = 15.1903(5)$  Å,  $c = 24.4754(7)$  (Å),  $\beta = 108.516(2)^\circ$ ,  $V = 8890.3(5)$  Å<sup>3</sup>). Also in this case the framework deviated slightly from  $C2/c$  symmetry and the observed symmetry lowering was ascribed to the TEA arrangement which is more favourable in the absence of a twofold crystallographic axis. In the next stage of ZSM-12-ASK-II refinement, the unit cell parameters obtained by whole powder pattern fitting (LeBail method) were refined to  $a = 25.0814(13)$  Å,  $b = 15.0987(8)$  Å,  $c = 24.4419(17)$  Å,  $\beta = 107.844(6)$ ,  $V = 8810.8(8)$  Å<sup>3</sup>. The goodness of fit parameters was reported in Table 1. The Rietveld procedure was initiated with the introduction of a partial structure model consisting of only the framework coordinates taken from Kasunic et al. [59].

The extra-framework sites were first located by difference Fourier maps and then optimized using the geometry optimization tool implemented in EXPO2014 (by plane wave DFT with dispersion correction, DFT-D). As reported by Smeets et al. [60] the location of organic guest species in

inorganic host structures from diffraction data is very complicated especially when organic compounds consist of light scatterers with low point symmetry, while their inorganic hosts consist of heavier scatterers and have high symmetry. Consequently, it difficult to “see” the organic guest, due not only to the difference in symmetry, but also to the disordering of guest molecule. For these reasons, this approach allowed us i) to minimize the energy of the crystal structure, ii) to provide reasonable bond lengths and angles and iii) to calculate the position of the H atoms. The resulting optimized structure was then used as input coordinates for GSAS and refined again together with the framework. This strategy has been repeated several times until the geometry of the molecule was reasonable and the structural model showed the best agreement with the experimental data. In order to secure a stable refinement, the azonia molecule coordinates were fixed in the final cycles of Rietveld refinement thus limiting the number of refined atomic displacement parameters.

The T–O mean distances are within the range expected for the silica framework ranging from 1.587 to 1.628 Å, respectively, the O–T–O angles range from 108.6° to 109.5°. The details of the refinement are given in Table 1, positional and thermal parameters for ZSM-12-ASK-II framework and extraframework atoms are in Table 1SI and Table 2SI, respectively.

On the basis of the Fourier difference maps, twenty partially occupied extra-framework sites were localized inside the 12MR (Figure 2). Ten of these (sites C1-C10 and N1, respectively) defined the position of AZO-1 molecule, the residual ones (sites C11-C20 and N2, respectively) that of the AZO-2 molecule (Figure 2). Therefore, the structure refinement gave an extraframework content of 6.13 azonia molecules per cell (corresponding to about 9.0% in weight) in good agreement with the weight loss given by the thermogravimetric analysis reported in Figure 3.

Figure 3 shows the TG/DTA curves of the ZSM-12-C sample for comparison [57]. The TG/DTA trace of ZSM-12-ASK-II sample highlighted a first weight loss (as well as endothermic peak in DTA) occurring at  $T < 120^{\circ}\text{C}$  which can be related to the desorption of physically adsorbed water from the surface (weight loss  $\approx 0.4\%$  dry wet/wet). The residual one ( $\approx 8.0\%$  dry wet/wet) comprises the SDA molecules degradation, in very good agreement with the results of X-ray diffraction data calculated on the basis of the refined occupancies. After SDA removal, the weight loss registered is related to the release of water adsorbed from both the surface (weight loss  $\sim 1.8\%$  dry wet/wet and DTA curve in the temperature range 25-  $105^{\circ}\text{C}$ ) and the channels (weight loss  $\sim 3.0\%$  dry wet/wet and DTA curves from  $105^{\circ}$  to  $900^{\circ}\text{C}$ ), respectively.

Refined azonia molecule positions suggested that their orientations did not maintain the twofold axes coinciding with the crystallographic twofold axis thus explaining the lowering space group symmetry to Cc. The final geometry of the azonia molecules was very close to ideal (Figure 4).

The refined bond distances revealed the occurrence of non-bonding interactions of both azonia molecules with the MTW pore wall in very good agreement with the molecular dynamics simulations reported by Millini et al. [44]. AZO-1 and AZO-2 molecules interact between them thus forming clusters aligned along the *b* axis (Figure 4).

## Conclusions

Some of the zeolite properties can be tuned during their synthesis by controlling crystal size and/or chemical composition, pore dimensions and their connectivity through the use of organic or inorganic structure-directing agents (SDAs). Computer modelling approaches have been developed to predict both position and conformation but only less frequently, diffraction techniques are used as tool to obtain structural informations concerning their long-range ordering. Uncertainties or ambiguities often persist due to the occurrence of very disordered local bonding geometries nevertheless, experimental evidences are mandatory to compare and eventually validate the computational models.

In this paper, pure-silica ZSM-12 (MTW topology) synthesized with 6-azonia-spiro-[5,5]-undecane template was carefully characterized by using X-ray synchrotron powder diffraction data. The structure refinement led to a monoclinic unit cell (space group *Cc*, *Z*=4, *a* = 25.0814(13) Å, *b* = 15.0987(8) Å, *c* = 24.4419(17) Å,  $\beta$  = 107.844(6), *V* = 8810.8(8) Å<sup>3</sup>) with a three times enlargement of the unit cell along the *b* axis with respect to that of the calcined starting ZSM-12 (space group *C2/c*, *Z*=1, *a* = 24.8633(3) Å, *b* = 5.01238(7) Å, *c* = 24.3275(7) Å,  $\beta$  = 107.7215(6)°). The structure refinement gave an extraframework content 6.13 azonia molecules per unit cell (corresponding to about 9.0% in weight) in good agreement with the weight loss given by the thermogravimetric analysis. The SDAs conformation and position in the framework structure did not maintain the twofold axes coinciding with the crystallographic twofold axis thus changing the space group symmetry from *C2/c* to *Cc*. The refined bond distances revealed the occurrence of non-bonding interactions of both azonia molecules with the MTW pore wall in very good agreement with the molecular dynamics simulations [44]. AZO-1 and AZO-2 molecules interact between them thus forming clusters aligned along the *b* axis. This information is crucial to clarify the role played by SDAs during the synthesis, to tailor the physicochemical properties of zeolites as well as to address their hydrophobicity, pore dimensions and cavities thus optimizing the selectivity of zeolite catalysts.

## Acknowledgements

This work was carried out in the framework of the project Protecting the Enclosed Parts of the Sea in Adriatic from pollution, PEPSEA (Project ID: 10047424) within the Interreg V A Italy Croatia Cross-border Cooperation Programme 2014-2020. PRIN project ZAPPING (PRIN2015 Prot.2015HK93L7) funded by the Italian MIUR is also acknowledged for funding. Authors thank Elisa Rodeghero and Giuseppe Nunziante for the help X-ray diffraction data collection.

## References

- [1] M. Kubů, R. Millini, & N. Žilková, *Catal. Today*, 324 (2019) pp. 3-14.
- [2] J. Čejka, G. Centi, J. Perez-Pariente & W. J. Roth *Catal. Today*, 179 (2012) pp. 2-15.
- [3] B. M. Weckhuysen & J. Yu, *Chem. Soc. Rev.*, 44 (2015) pp. 7022-7024.
- [4] A. Corma, *Angew. Chem. Int. Ed.*, 55 (2016) pp. 6112-6113.
- [5] J. D. Rimer, *Nat. Catal.*, 1 (2018) pp 488-489.
- [6] M. Moliner, F. Rey & Corma, A., *Angew. Chem. Int. Ed.*, 52 (2013) pp.13880-13889.
- [7] M. Hernández-Rodríguez, J. L. Jordá, F. Rey & A. Corma, *J. Am. Chem. Soc.*, 134 (2012) pp. 13232-13235.
- [8] H. Gies, in: *Inclusion Phenomena*, J. Atwood, E. Davies, J. McNicol (Eds.), 5 Oxford University Press, Oxford. 1991, pp. 1–5.
- [9] H. Gies, & B. Marler, *Zeolites*, 12 (1992) pp. 42–49.
- [10] J. Li, A. Corma & J. Yu, *Chem. Soc. Rev.*, 44 (2015) pp. 7112-7127.
- [11] A. Navrotsky, O. Trofymuk, & A. A. Levchenko, *Chem. Rev.*, 109 (2009) pp. 3885-3902.
- [12] Corma, M. J. Diaz-Cabanas, J. L. Jorda, F. Rey, G. Sastre, K. G. Strohmaier, *J. Am. Chem. Soc.* 130, (2008) 16482 –16483.
- [13] R. Millini, G. Perego, W. O. Parker, Jr., G. Bellussi, L. Carluccio, *Microporous Mater.*, 4 (1995) 221-230.
- [14] M. Moliner, F. Rey, A. Corma, *Angew. Chem., Int. Ed.*, 52 (2013) pp. 13880–13889.

- [15] T. Davis, T. Drews, H. Ramanan, C. He, J. Dong, H. Schnablegger, M. Katsoulakis, E. Kokkoli, A. McCormick, R. Penn, M. Tsapatsis, *Nat. Mater.* 5 (2006) pp. 400–408.
- [16] S. M. Auerbach, M. H. Ford, P. A., *Curr. Opin. Colloid Interface Sci.*, 10 (2005) pp. 220–225.
- [17] S. M. Auerbach, W. Fan, P. A., *Int. Rev. Phys. Chem.*, 34 (2015) pp. 35–70.
- [18] O. V. Shvets, N. Kasian, A. Zukal, J. Pinkas, J. Cejka, *Chem. Mater.*, 22 (2010) pp. 3482–3495.
- [19] M. N. Khan, S. M. Auerbach & P. A. Monson, *J. Phys. Chem. C*, 119 (2015) pp. 28046–28054.
- [20] D. W. Lewis, D. J. Willock, C. R. A. Catlow, G. J. Hutchings, J. M. Thomas, *Nature*, 382 (1996) pp. 604–606.
- [21] D. W. Lewis, C. M. Freeman, C. R. A. Catlow, *J. Phys. Chem.*, 99 (1995) pp. 11194–11202.
- [22] D. W. Lewis, C. R. A. Catlow, J. M. Thomas, *Chem. Mater.*, 8 (1996) pp. 1112–1118.
- [23] A. P. Stevens, A. M. Gorman, C. M. Freeman, P. A. Cox, *J. Chem. Soc., Faraday Trans.*, 92 (1996) pp. 2065–2073.
- [24] D. W. Lewis, C. R. A. Catlow, J. M. Thomas, *J. M. Faraday Discuss.*, 106 (1997) pp. 451–471.
- [25] P. A. Cox, J. L. Casci, A. P. Stevens, *Faraday Discuss.*, 106 (1997) pp. 473–487.
- [26] R. A. Catlow, L. Ackerman, R. G. Bell, D. H. Gay, S. Holt, D. W. Lewis, M. A. Nygren, G. Sastre, D. C. Sayle, P. E. Sinclair, *J. Mol. Catal. A: Chem.*, 115 (1997) pp. 431–448.
- [27] A. J. Ramirez-Cuesta, P. C. H. Mitchell, P. M. Rodger, *J. Chem. Soc., Faraday Trans.*, 94 (1998) pp. 2249–2255.
- [28] G. Sastre, S. Leiva, M. J. Sabater, I. Giménez, F. Rey, S. Valencia, A. Corma, *J. Phys. Chem. B*, 107 (2003) pp. 5432–5440.
- [29] S. I. Zones, Y. Nakagawa, L. T. Yuen, T. V. Harris, *J. Am. Chem. Soc.*, 118 (1996) pp. 7558–7567.
- [30] S. I. Zones, Y. Nakagawa, G. S. Lee, T. V. Harris, L. T. Yuen, *Micro. Meso. Mater.*, 22 (1998) pp. 69–85.
- [31] S. I. Zones, C.-Y. Chen, L. W. Finger, R. C. Medrud, C. L. Kivi, P. A. Crozier, I. Y. Chan, T. V. Harris, L. W. Beck, *Chem. Eur. J.*, 4 (1998) pp. 1312–1323.



- [32] S. I. Zones, US Pat., 4 (1985) 510, 256 A.
- [33] Carluccio, R. Millini, G. Bellussi, Eur. Patent 796 (1997) 821.
- [34] A. Losurdo, W. Y. Wen and C. Jolicoeur, *J. Solution Chem.*, 8 (1979) pp. 449–460.
- [35] Corma and A. Martinez, *Adv. Mater.*, 7 (1995) pp. 137–144.
- [36] T. F. Degnan, *Top. Catal.*, 13 (2000) pp. 349–356.
- [37] Yilmaz and U. Müller, *Top. Catal.*, 52 (2009) pp. 888–895.
- [38] A. Corma, F. Rey, S. Valencia, J. L. Jorda and J. Rius, *Nat. Mater.*, 2 (2003) pp. 493–497.
- [39] Sastre, R. Pulido Castañeda and A. Corma, *J. Phys. Chem. B*, 108 (2004) pp. 8830–8835.
- [40] F. Frigerio, L. Carluccio, W. O’Neil Parker Jr and R. Millini, *J. Mol. Catal. A Chem.*, 166 (2001) pp. 167–174.
- [41] J.-L. Paillaud, Y. Lorgouilloux, B. Harbuzaru, P. Caullet, J. Patarin and N. Bats, *Stud. Surf. Sci. Catal.*, 170 (2007) pp. 389–396.
- [42] R. Yuan, Na. Claes, E. Verheyen, A. Tuel, S. Bals, E. Breynaert, J. A. Martensa and C. E. A. Kirschhock, *New J. Chem.*, 40 (2016) pp. 4319–4324.
- [43] D. Yuhas, J. P. Mowat, M. A. Miller & W. Sinkler, *Chem. Mat.*, 30 (2018) pp. 582–586.
- [44] R. Millini, L. Carluccio, F. Frigerio, W. O. Parker and G. Bellussi, *Micropor. Mesopor. Mat.*, 24 (1998) pp.199–211.
- [45] S. Zanardi, G. Cruciani, L. C. Carluccio, G. Bellussi, C. Perego & R. Millini, *Angew. Chem. Int. Ed.*, 41 (2002) pp. 4109–4112.
- [46] S. Zanardi, G. Cruciani, L. C. Carluccio, G. Bellussi, C. Perego & R. Millini, *J. Porous Mat.*, 14 (2007) pp. 315–323.
- [47] S. Zanardi, R. Millini, F. Frigerio, A. Belloni, G. Cruciani, G. Bellussi, A. Carati, C. Rizzo & E. Montanari, *Micropor. Mesopor. Mat.*, 143 (2011) pp. 6–13.
- [48] G. Bellussi, R. Millini, P. Pollesel & C. Perego, *New J. Chem.*, 40 (2016) pp. 4061–4077.
- [49] L. Rebuffi, J. R. Plaisier, M. Abdellatif, A. Lausi, P. Scardi, *Z. Anorg. Allg. Chem.*, 640 (2014) pp. 3100–3106.

- [50] J. R. Plaisier, L. Nodari, L. Gigli, E. P. Rebollo San Miguel, R. Bertonecello, A. Lausi, *Acta Imeko*, 6 (2017) pp. 71-75.
- [51] A. Altomare, C. Cuocci, C. Giacobozzo, A. Moliterni, R. Rizzi, N. Corriero, A. Falcicchio, *J. Appl. Cryst.* 46 (2013) pp. 1231-1235.
- [52] A. Le Bail, H. Duroy & J.L. Fourquet, *Mat. Res. Bull.* 23 (1988) pp. 447-452.
- [53] A.C. Larson and R.B. Von Dreele, "General Structure Analysis System (GSAS)", Los Alamos National Laboratory Report LAUR (2000) 86-748.
- [54] B. H. Toby, EXPGUI, a graphical user interface for GSAS, *J. Appl. Cryst.* 34 (2001) pp. 210-213.
- [55] L. W. Finger, D. E. Cox, & A. P. Jephcoat, *J. Appl. Cryst.*, 27 (1994) pp.892-900.
- [56] van Laar, W.B.Yelon, *J. Appl. Cryst.*, 17 (1984) pp. 47-54.
- [57] Rodeghero, L. Pasti, G. Nunziante, T. Chenet, L. Gigli, J. R. Plaisier, & A. Martucci, *Am. Mineral.*, 104 (2019) pp. 317-324.
- [58] C.A. Fyfe, H. Gies, G.T. Kokotailo, B. Marler and D. E. Cox, *J. Phys. Chem.*, 94 (1990) pp. 3718-3721.
- [59] M. Kasunić, J. Legiša, A. Meden, N. Zabukovec Logar, A. M. Beale, A. Golobič, *Micropor. Mesopor. Mat.*, 122 (2009) pp. 255–263.

### Figure captions

Figure 1. Representative powders pattern for ZSM-12-c (blue) and ZSM-12-ASK-II (black) respectively (a). ZSM-12-ASK-II observed (crosses), calculated (green line), Bragg diffraction peaks (vertical bars) and the difference profile (violet line) obtained by GSAS evaluation program (b).

Figure 2. ZSM-12-ASK-II structure view along [001] and [010], respectively.

Figure 3 TG (a) and DTA (b) curves for ZSM-12-C (blue) and ZSM-12-ASK-II (red), respectively.

Figure 4. Clusters of AZO-1 and AZO-2 molecules.