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Green and cost-effective synthesis of the superconductor BSCCO (Bi-2212), using a natural deep eutectic solvent.

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ABSTRACT: Ionic liquids/Deep eutectic solvents have been extensively utilized in many different areas however, these systems have not been widely used for their chelating properties in the synthesis of phase pure metal oxides. This mainly due to the high cost of the ionic liquid and the lack of ability to solubilize some water-insoluble metal salts, such as bismuth nitrate. Here we present for the first time the use of a cost-effective natural deep eutectic solvent (NADES), namely betaine:D-(+)-glucose which is capable of solubilizing these insoluble metal salts and produce after calcination, high yields (>90 %) of a quinternary, superconducting metal oxide. Moreover, the stability over time of the natural deep eutectic solvent and how this affects the overall outcome of the synthesis is discussed.

1. Introduction

The history of ionic liquids date back to when the first ionic liquid was synthesized by Walden in 1914;[1] namely ethyl ammonium nitrate (EAN), by neutralizing ethyl-amine with concentrated HNO_3. It was not until 1951 when the second generation of ionic liquids formed by mixing alkyl pyridinium chlorides with $AlCl_3$ were reported by Hurley and Wier.[2] The main drawback of this combination is the fact that the resulting solvent is moisture sensitive and the pH hard to control.[3] However, an advance

was made when in 1992 the first moisture and air-stable ionic liquids were made. These solvents, reported by Wilkes and Zaworotko[4] are based on imidazolium and tetrafluoroborate, and due to their novel properties, these systems started to receive broad attention in the scientific community.

With the establishment of the concept of green chemistry in the early 1990's, ionic liquids took a priority place worldwide as promising alternative solvents.[5] Moreover, the variety of properties shown by these compounds such as extremely low vapour pressure, high tuneability, nonflammability, wide solubility and high stability[6] have made them great candidates as gas absorbents,[7] lubricants,[8] catalysts,[9] extractants,[10] ionic liquid crystals[11] and chelators.[12,13]

Ionic liquids were initially classified as green however, such an attribution has been recently been called into question.[14] Several studies pointed out the hazardous toxicity and very low biodegradability of most ILs.[15,16] To obtain the desired functionality, ionic liquids must be of high purity otherwise their properties are compromised. In addition to this, the synthesis of ILs require large amount of salts and solvents to ensure complete ion exchange. Collectively the syntheses of some ILs are very far away from being environmentally friendly and the synthetic complexity is also reflected in the high price of common ILs.[17]

In 2001 a new generation of solvents emerged, namely deep eutectic solvents, firstly synthesized by P. Abbott.[18] Deep eutectic solvents overcome all the drawbacks that the ionic liquids have due to a straightforward synthesis by only mixing together components capable of forming an eutectic mixture. Two of the most common compounds used are choline chloride and another quaternary ammonium salt, both of which are green, cheap, renewable and biodegradable.

Deep eutectic solvents exhibit similar physico-chemical properties to the ionic liquids and as a result these compounds are commonly considered as ionic liquids in the literature. However, deep eutectic solvents differ in the fact that they are not always formed only by ionic species and, in fact, can be made by non-ionic species.[17] Many deep eutectic constituents have been explored[19,20] and include the use of natural products such as organic acids, amino acids and sugars.[19,21,22] Molecules used by nature are

perfect candidates to produce new and green deep eutectic solvents, also their vast diversity provides different chemical properties.

From previous experiments,[23] it was determined that the presence carbonyl groups in the ionic liquid/deep eutectic solvent leads, during the calcination process, towards the formation of carbonate phases when heated in the presence of cationic metal species. The fact that carbonate phases can then subsequently decompose releasing $CO_{2(g)}$ allows a faster re-integration of metal ions to the synthetic process facilitating recombination and thus forming the desired crystal composition, whereas without CO_3^{2-} the synthesis will proceed via solid state reactions until the final inorganic phase composition is reached. Furthermore, it is important to exclude any solvent which contains extra elements that can take part in the reaction process, such as chlorine. In the same report[23] it was demonstrated that elements like chlorine will form crystal phases which if stable at high temperature, will entirely disrupt the formation of the targeted phase. Therefore, following this principle and to lower the overall expenses of the synthetic process, namely substituting 1-ethyl-3-methylimidazolium acetate and 1-ethyl-3-methylimidazolium nitrate, a good candidate for the successful synthesis of a complex inorganic phase proposed was a NADES made by mixing betaine and D-(+)-glucose in 5:2 molar ratio. This NADES was employed for the synthesis of $Bi_2Sr_2CaCu_2O_{8+x}$ (BSCCO or Bi-2212) a high-temperature superconductor. Previous work[13] done to synthesise this crystal composition required prior preparation to integrate barium nitrate, an insoluble salt, into a solution. To achieve that ethylenediaminetetraacetic acid (EDTA) and ammonium hydroxide were used. Furthermore, instead of 1-ethyl-3-methylimidazolium acetate, 1-ethyl-3-methylimidazolium nitrate was utilized,[13] which is extremely expensive. In contrast, via the use of betaine it was possible to solubilize bismuth nitrate in water, therefore avoiding these expensive previous steps.

2. Material and methods

Betaine (BioUltra, ≥99.0% (NT)), D-(+)-glucose (≥99.5% (GC)), bismuth nitrate pentahydrate (99.99%), strontium nitrate (99%), and calcium nitrate tetrahydrate (≥99.0%), copper nitrate hemipentahydrate (99.99%) were purchased from Sigma-Aldrich UK. Deionized water was obtained using a MilliQ PureLab Ultra (18.2 M Ω cm^{-1}). None of the materials required further purification and were used as received.

2.1. Generation of deep eutectic solvents

Betaine 5:2 D-(+)-glucose DES was synthesized by mixing both solids in the stated molar ratio, 3 g with 1.8453 g respectively. After that, water (6.336 ml) was added to allow the mixture of such with a final volume of 10 ml. The complete mixture will start forming after a few minutes under strong agitation.

2.2. Generation of aqueous precursors

Calcium nitrate tetrahydrate (0.05 M), 0.2116 g strontium nitrate (0.1 M), and 0.2326 g copper nitrate hemi(pentahydrate) (0.1 M) were mixed in a vial with 10 ml DI water under stirring until all salts dissolved, forming a light blue solution.

2.3. Generation of deep eutectic-based precursors

Solutions were prepared by mixing bismuth nitrate (0.242 g, 0.1 M) in 5 ml of DES. Then, 1 ml of betaine/bismuth solution was then added to 1 ml of the rest of metal nitrates solution plus an extra 1.05 ml of betaine: D-(+)-glucose DES solution. The final volume ratio was 0.75:1 v/v betaine: D-(+)-glucose DES/metal nitrate solution. The mixture was then heated at 70 °C for 2 hours to allow full dehydration. After complete dehydration a gel will be obtained therefore there is no need to add extra poly-chelating agents.

2.4. Heating protocols

Dehydrated precursors were calcined immediately after preparation in air in crucibles for 2 h with a heating ramp rate of 5 °C min $^{-1}$ at 850 °C. For temperature analysis samples were calcined from 350 °C to 750 °C in steps of 100 °C, and from 775 °C to 850 °C in steps of 25 °C.

2.5. Characterization

For the characterization of the samples TEM analysis was carried out on JEOL JEM 1400EX microscope. SEM samples were analysed on JEOL JSM 5600LV with Oxford energy dispersive X-ray detector. Powder X-ray diffraction (pXRD) was carried out on Bruker D8 Advance diffractometer (CuKα 1 radiation at λ = 1.54056 Å) equipped with a Lynx-eye position sensitive detector. Rietvield analysis was done via Profex 3.12.1 Software.[24] Superconducting properties were investigated using DC magnetic susceptibility measurements with a SQUID (superconducting quantum interference device) magnetometer (Quantum Design MPMS-XL) equipped with a 5 T superconducting magnet. Samples were run under in zero-field cooling (ZFC) and 50 Oe field-cooling (FC) conditions with temperature ranges of 20 - 100 K. Unless specified in the figure legends, samples for these physical characterisations were carried out using Bi-2212 synthesized using freshly prepared betaine: glucose DES. Diffraction patterns were analysed using the Inorganic Crystal Structure Database (ICSD) reference numbers for phase identification (supplementary information Table S1). When required, pelletised samples of 1 cm diameter were produced using a pressing force of 2000 kg effective mass.

3. Results and discussion

3.1. Infrared spectroscopy

By FTIR it is possible to track the first interactions between the chelating agent and the metal cations. The FTIR study was done by comparing the interaction of the NADES itself and with all the metal cations (M-NADES) before and after dehydration (Figure 1). Betaine comprises a carbonyl group

on one side of the molecule and a tri-substituted amine on the other side. Tertiary amines exhibit no bands in the FTIR therefore the focus relies on the range of wavelengths from 3300-2500 cm^{-1} belonging to the O-H stretching, 1630 cm^{-1} to the C=O stretching, 1325 cm^{-1} and 885 cm^{-1} to the O-H in plane bend [31] (Figure 1). Most of the bands remain at the same wavelength with the only one exception the band found in the rage from 2958 cm^{-1} to 2970 cm^{-1}. When the hydrated metal nitrates are introduced in the NADES the band is barely seen in the wavelength 2982 cm^{-1}, however, in comparison it is not visible for the NADES itself. Furthermore, when the M-NADES is dehydrated the band is clearly visible at wavelengths 2981cm^{-1} and 2971cm^{-1} The fact that all the other remaining bands corresponding to the carboxyl group are not shifted towards any directions implies that the band seen in the range of 2958 cm^{-1} to 2970 cm^{-1} belong to the nitrate groups of the metal cations [25,26] rather than the carboxyl group of the betaine. Overall, in contrast with what was observed previously when (emim)OAc was used[23], there is not complex formation between the molecule betaine and the metal cations, but rather pure electrostatic interactions which, would explain the lack of a shift in any band of the carboxyl group of the betaine
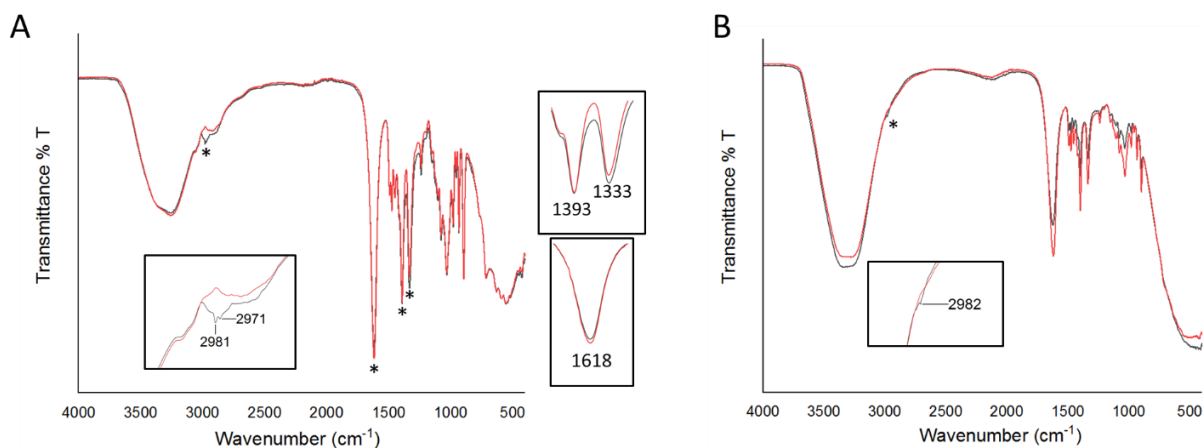
Figure 1. Fourier transformation infrared spectra of A) Black. - NADES with metal cations, and Red.- just NADES both dehydrated. B) Fourier transformation infrared spectra of A.- Black. - NADES with metal cations, and Red.- just NADES both hydrated. Inset represent zoom areas of the respective bands marked with *.

molecule or the appearance of a new band due to the complex formation. Moreover, these purely electrostatic interactions can be observed by changes in the width of the infrared bands due to the number of chemical environments (Figure 1 A).
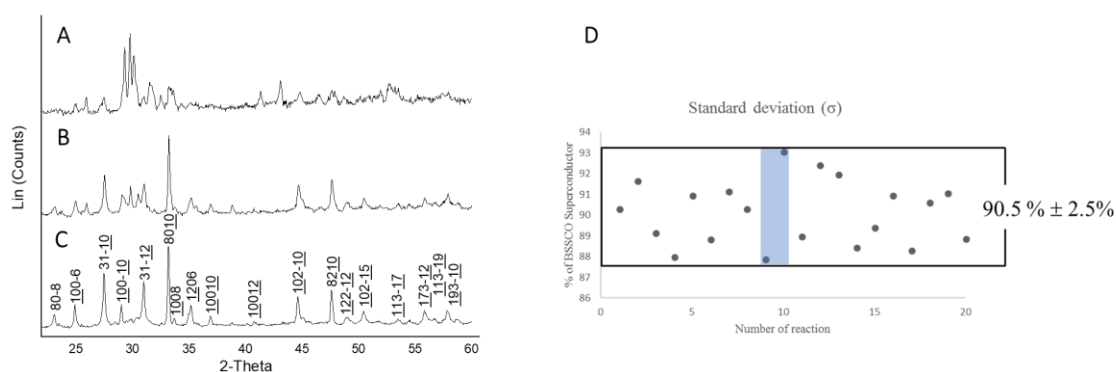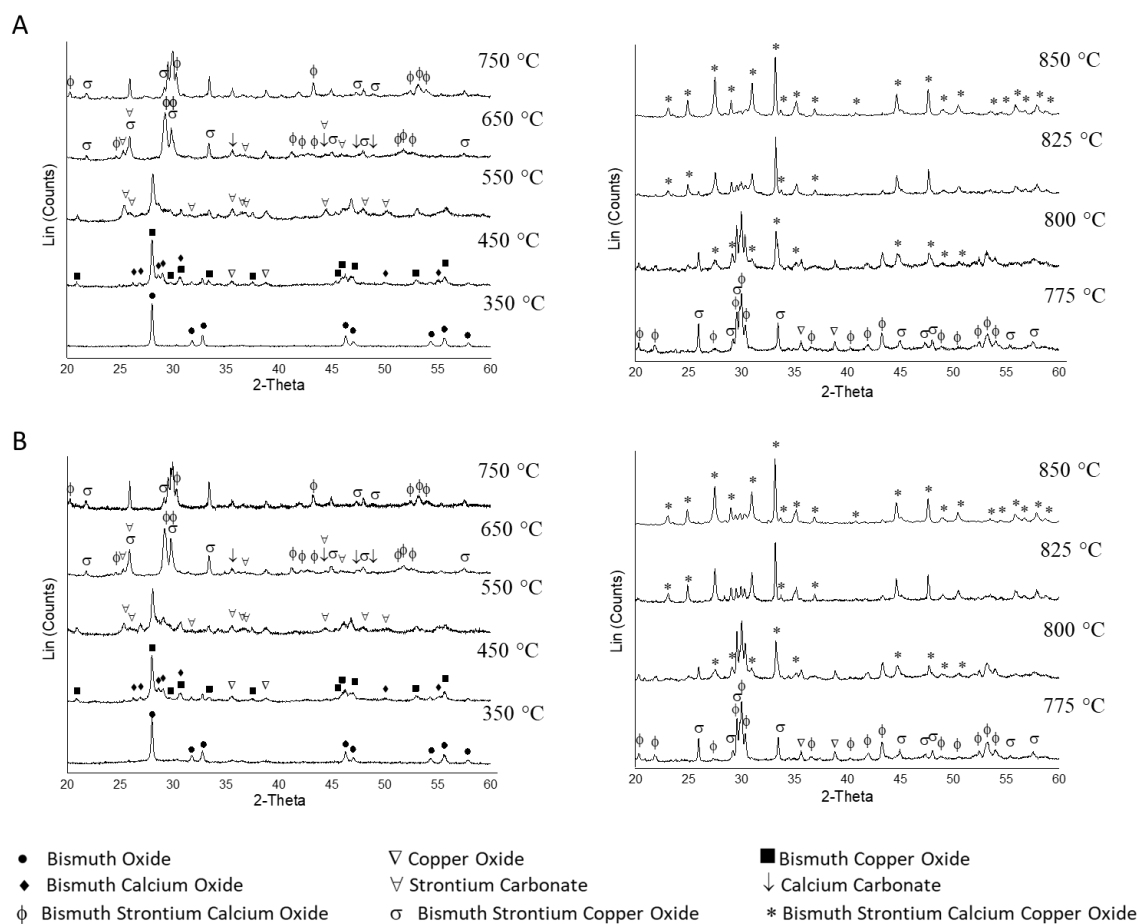
3.2. Temperature analysis

Control reactions were undertaken to understand the role played by every component that forms part of the synthesis, namely glucose, betaine, and finally the NADES. With the use of pXRD (Figure 2) it was established that just the mixture of betaine and glucose (Figure 2 C), will provide high yields of BSCCO superconductor. Nonetheless, using only betaine (Figure 2 B) as a mono-molecular chelating agent could produce, based on Rietvield refinement, 82.9 % of the superconductive phase, whereas the reaction carried out with D-(+)-glucose (Figure 2 A) gave only 22.5 %.

DESs are not yet fully-characterised systems and their stability has been subject of study[27], therefore the analysis of the reaction over a period of time, for 21 days every 3 days (Supplementary information Figure S1), was performed. The reaction performed immediately after producing the NADES gave 93 % of the desired crystal phase (Figure 2 C), this being the optimum result obtained. 20 reactions followed to truly prove the reproducibility of this synthesis, giving an average value of 90.5% ± 2.5 % of the superconducting phase (Figure 2 D). After the third day there was a drop in the percentage of the target Bi-2212 phase to 87.3 % and a further decrease to 81.7 % by the sixth day and all days after that. DES are highly interactive systems capable of forming complex structures via hydrogen-bonding networks,[6,17,28,29] however, continuous interaction between components can also occur, producing a chemical structure change of a component therefore, changing the chelating properties of the DES. In the case of betaine: glucose based on the powder x-ray diffraction patterns, is notorious after 6 days of aging.


Figure 2. Powder X-ray diffraction pattern of the synthesis of Bi-2212 using A) Glucose, B) Betaine, and C) Betaine: D-(+)-glucose (5:2) NADES as chelating agents

To elucidate what was happening during the synthetic process, temperature analyses via pXRD (Figure 3 & 4) were undertaken. The crystal growth can be described in five different stages. The first part of the reaction (Figure 4 gray) shown singular metal oxides, mainly bismuth oxide (Bi_2O_3) and barely detectable diffractions belonging to copper oxide (CuO). The second period (Figure 4 blue) is represented by the appearance of ternary metal oxides, bismuth copper oxide (Bi_2CuO_4) and bismuth calcium oxide ($Bi_{0.80}Ca_{0.20}O_{1.19}$). At this point there is not yet a crystalline phase containing strontium. The third period (Figure 4 red) covers the inception of carbonate phases such as strontium carbonate ($Sr(CO_3)$), calcium carbonate ($Ca(CO_3)$) and strontium calcium carbonate ($Sr_{0.50}Ca_{0.50}(CO_3)$). The fourth and last period (Figure 4 green) is significantly important as it represents the growth and evolution of the more complex quaternary phases, such as bismuth strontium calcium oxide ($Bi_6Sr_{6.27}Ca_{4.73}O_{22}$) and bismuth strontium copper oxide ($Bi_{1.91}Sr_{1.84}CuO_{5.48}$); the emergence of those crystal phases can be deduced as being due to the continuous decomposition of the carbonates and the constant reaction of the ternary crystal phases. In this period is also where the desired superconducting phase is first detected, at


Figure 3. Temperature Analysis via powder X-ray diffraction patterns of the synthesis of Bi-2212 using A) freshly made NADES, and B) aged for 21 days NADES.
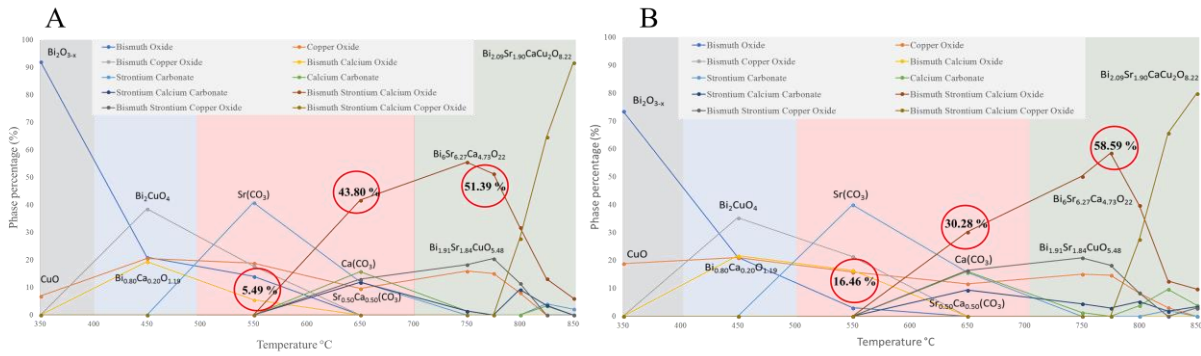
Figure 4. A) Graphical representation via qualitative analysis of pXRD patterns from the temperature analysis of the synthesis of Bi-2212 using A) Immediately prepared NADES, and B) NADES aged for 21 days.

775 °C, and ending at 850 °C with the final crystal composition of Bi-2212. From this period is clearly defined that the precursory phases needed for the generation of the superconductive phase are bismuth strontium copper oxide, bismuth strontium calcium oxide, and copper oxide. A schematic representing the crystal growth can be found in Figure 5.

The crystal growth in both conditions, when the NADES was freshly made and after 21 days of aging, appeared similar from pXRD results (Figure 3), however after doing a concise analysis with Rietvield refinement, a stark difference can be observed. Highlighted in Figure 4, it is noticeable that the when the NADES is freshly prepared, bismuth calcium oxide reacts faster than after the solution is left for days, change is observable in values changes from 19.3 % at 450 °C to 5.4 % at 550 °C, whereas after the solution is aged, the percentage drops from 21.7 % at 450 °C to 16.4 % at 550°C. This will have a significant impact in the synthesis of Bi-2212 because the precursory quaternary phases are produced from the elements released from the decay of the carbonates and the recombination of ternary crystal phases. The implication of this is graphically seen for bismuth strontium calcium oxide, where when the NADES is freshly prepared, it is present as 43.8 % at 650 °C of the total percentage, and only 30.28 % at the same temperature when the solvent was aged for 21 days; consequently, the crystal phase will start to re-combine 25 °C earlier in the first case. This will eventually result in >90 % of the superconducting phase against 81 % ± 5 % from an aged solution.
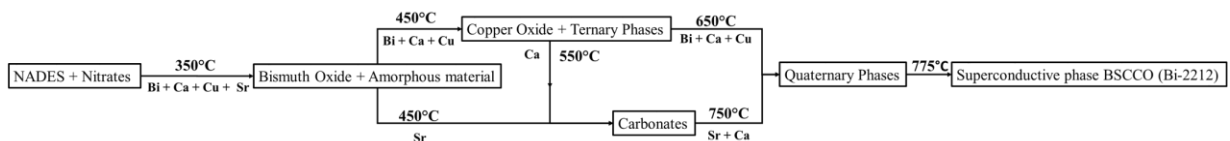
Figure 5. Diagram of the crystal growth of the synthesis of Bi-2212 using NADES.

### 3.3. Structural characterization

3.3.1. SEM and TEM

Characterization via TEM and SEM showed that in both cases neither the micro- or macromorphology was controlled in any significant way. The usual Bi-2212 structures that are found in typical control syntheses are present, namely that the material is mainly composed by planar crystallites at the microscale (Figure 6 A), albeit the macrostructure resembles a sponge-like morphology made of polycrystalline aggregates. (Figure 6 B), presumably as a result of the outgassing of the NADES as it decomposes.

SEM-EDXA showed a homogenous distribution, throughout all the material, of all the metal cations involved in the reaction (Figure 6 B).

3.3.2. Squid magnetometry

SQUID magnetometry (Figure 6 C), measuring the magnetic susceptibility as a function of temperature, showed that the critical temperature at which the sample starts to exhibit a superconducting state, T_c onset, was 82 K. This compares favourably with the usually reported T_c onset for Bi-2212 as being between 82 K and 90 K.[30,31]
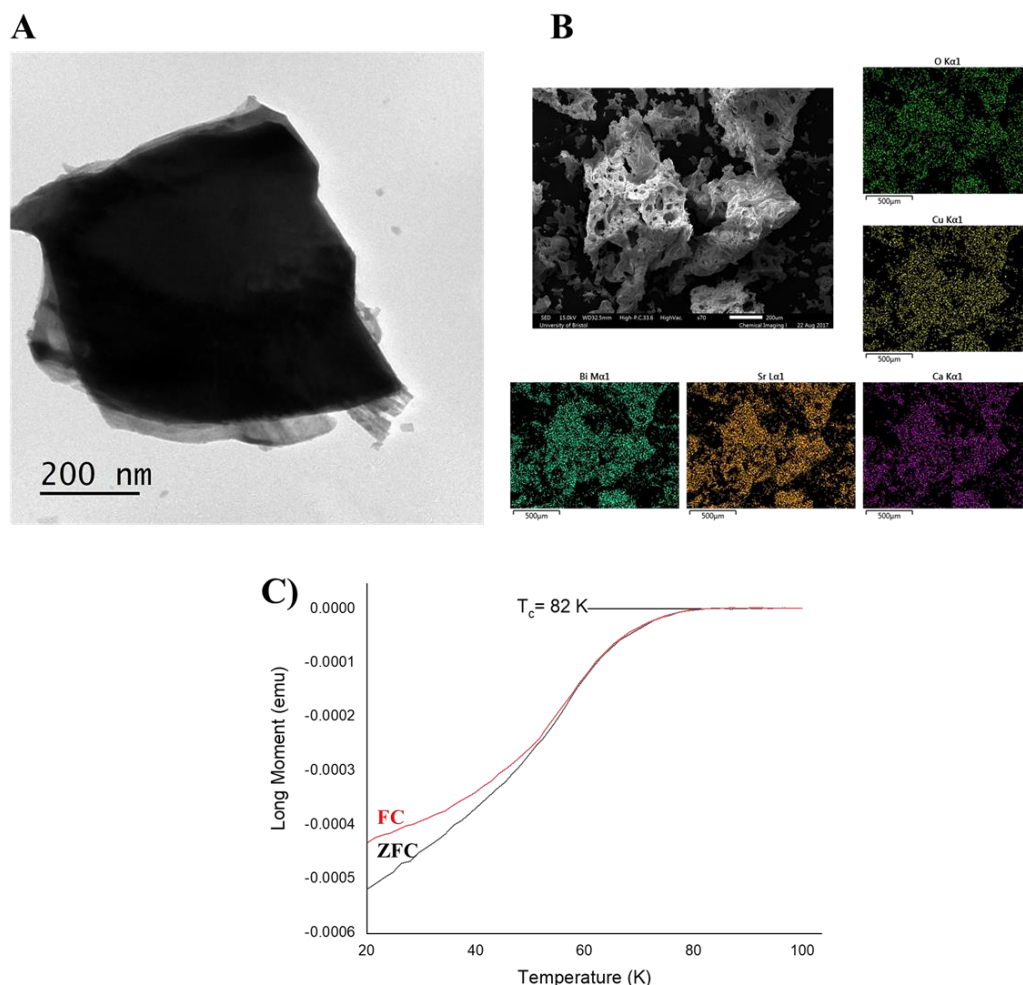
Figure 6. A) Transmission electron microscopy of Bi-2212 nanocrystals, and B) Scanning electron microscopy of Bi-2212 with the elemental mapping of each respective element involved, and C) SQUID characterization of Bi-2212 synthesized using freshly prepared NADES.

4. Conclusions

The use of betaine as a mono-nonspecific chelating molecule, proven to be non-specific via FTIR, in a deep eutectic solvent allows the dissolution of bismuth nitrate (Supplementary information Figure S2), leading to the formation of a uniform multicationic solution in the NADES. The even distribution allowed, after calcination, the creation of the superconductor Bi-2212 by a NADES for the first time. Through this synthetic protocol it was possible to obtain > 90 % of the superconducting crystal composition. However, it was noted that after 6 days of aging of the NADES solution, a considerable growth of precursory phases instead of the superconductive crystal composition occurred. There is evidently a continuous interaction of the polysaccharide and betaine, this phenomenon can be also visually observed by pictures taken at different times, namely freshly prepared being a transparent solution, after 2 months with a yellow coloration, and after 6 months turning into a dark yellow

(Figure 7). Such changes can be related to the oxidation of the polysaccharide over time therefore, changing the chelating properties of the molecule.

Figure 7. Optical image of the NADES freshly prepared (A), 2 months aged (B), and 6 months aged (C)

Certainly, further investigation is needed to provide more evidence of such process and how is that directly related to the change in the chelating properties of the DES. However, based on this observation should provide valuable guidance to those wishing to use deep eutectic solvents in the synthesis of complex functional materials, in that syntheses should be attempted within the first 48 hours of preparation of the DES to avoid any structural changes of the solvent.

5. Associated content

5.1. Supporting Information.
Powder X-ray diffraction patterns tracking changes every 3 days attempting the synthesis of Bi-2212 superconductor. Optical images showing the dissolution of bismuth nitrate in D-(+)-glucose and in betaine. Table containing all the ICSD card numbers used for Rietvield refinement.

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5.2.2. Author Contributions

All authors have given approval to the final version of the manuscript.

5.3. Funding Sources

5.4. Acknowledgments

5.5. Abbreviations

NADES, Natural deep eutectic solvent. Bi-2212, $Bi_2Sr_2CaCu_2O_{8+x}$.

Bibliography

[1]   P. Walden, eber die Molekulargro¨sse und Elektrische Leitfa¨higkeit Einiger Geschmolzenen Salze, Bull.
       Acad. Imp. Sci. St.- Petersbourg, Ser. . 8 (1914) 405 − 422.
       http://www.mathnet.ru/php/archive.phtml?wshow=paper&jrnid=im&paperid=6491&option_lang=rus
       (accessed June 8, 2018).

[2]   F.H. Hurley, T.P. WIer, The Electrodeposition of Aluminum from Nonaqueous Solutions at Room
       Temperature, J. Electrochem. Soc. 98 (1951) 207. doi:10.1149/1.2778133.

[3]   M. V. Fedorov, A.A. Kornyshev, Ionic Liquids at Electrified Interfaces, Chem. Rev. 114 (2014) 2978–
       3036. doi:10.1021/cr400374x.

[4]   J.S. Wilkes, M.J. Zaworotko, Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids, J.
       Chem. Soc. Chem. Commun. 0 (1992) 965. doi:10.1039/c39920000965.

[5]   R.D. Rogers, K.R. Seddon, S. Volkov, Green Industrial Applications of Ionic Liquids, Springer
       Netherlands, 2003.
       https://books.google.co.uk/books?hl=en&lr=&id=6GJsCQAAQBAJ&oi=fnd&pg=PR11&dq=Green+Indu
       strial+Applications+of+Ionic+Liquids,+ed.+R.+Rogers,+K.+Seddon+and+S.+Volkov,+Springer,+2003&
       ots=QqvMsQeoec&sig=PzjeME5BycjE8_MhwBP0tWuVFfI#v=onepage&q&f=false (accessed June 8,
       2018).

[6]   Z. Ma, J. Yu, S. Dai, Preparation of Inorganic Materials Using Ionic Liquids, Adv. Mater. 22 (2010) 261–
       285. doi:10.1002/adma.200900603.

[7]   G. García, S. Aparicio, R. Ullah, M. Atilhan, Deep Eutectic Solvents: Physicochemical Properties and Gas
       Separation Applications, Energy & Fuels. 29 (2015) 2616–2644. doi:10.1021/ef5028873.

[8]   A.P. Abbott, E.I. Ahmed, R.C. Harris, K.S. Ryder, Evaluating water miscible deep eutectic solvents
       (DESs) and ionic liquids as potential lubricants, Green Chem. 16 (2014) 4156–4161.
       doi:10.1039/C4GC00952E.

[9]   P. Liu, J.-W. Hao, L.-P. Mo, Z.-H. Zhang, Recent advances in the application of deep eutectic solvents as
       sustainable media as well as catalysts in organic reactions, RSC Adv. 5 (2015) 48675–48704.
       doi:10.1039/C5RA05746A.

[10]   Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Ionic Liquids and Deep Eutectic

Solvents in Natural Products Research: Mixtures of Solids as Extraction Solvents, J. Nat. Prod. 76 (2013) 2162–2173. doi:10.1021/np400051w.

[11] A.P. Abbott, G. Capper, S. Gray, Design of Improved Deep Eutectic Solvents Using Hole Theory, ChemPhysChem. 7 (2006) 803–806. doi:10.1002/cphc.200500489.

[12] O. Gómez Rojas, G. Song, S.R. Hall, Fast and scalable synthesis of strontium niobates with controlled stoichiometry, CrystEngComm. 19 (2017) 5351–5355. doi:10.1039/C7CE01298E.

[13] D.C. Green, S. Glatzel, A.M. Collins, A.J. Patil, S.R. Hall, A New General Synthetic Strategy for Phase-Pure Complex Functional Materials, Adv. Mater. 24 (2012) 5767–5772. doi:10.1002/adma.201202683.

[14] M. Deetlefs, K.R. Seddon, Assessing the greenness of some typical laboratory ionic liquid preparations, Green Chem. 12 (2010) 17–30. doi:10.1039/B915049H.

[15] N. V. Plechkova, K.R. Seddon, Applications of ionic liquids in the chemical industry, Chem. Soc. Rev. 37 (2008) 123–150. doi:10.1039/B006677J.

[16] A. Romero, A. Santos, J. Tojo, A. Rodríguez, Toxicity and biodegradability of imidazolium ionic liquids, J. Hazard. Mater. 151 (2008) 268–273. doi:10.1016/J.JHAZMAT.2007.10.079.

[17] Q. Zhang, K. De Oliveira Vigier, S. Royer, F. Jérôme, Deep eutectic solvents: syntheses, properties and applications, Chem. Soc. Rev. 41 (2012) 7108. doi:10.1039/c2cs35178a.

[18] A.P. Abbott, G. Capper, D.L. Davies, H.L. Munro, R.K. Rasheed, V. Tambyrajah, Preparation of novel, moisture-stable, Lewis-acidic ionic liquids containing quaternary ammonium salts with functional side chains, Chem. Commun. 0 (2001) 2010–2011. doi:10.1039/b106357j.

[19] Y. Dai, J. van Spronsen, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Natural deep eutectic solvents as new potential media for green technology, Anal. Chim. Acta. 766 (2013) 61–68. doi:10.1016/J.ACA.2012.12.019.

[20] Y. Dai, G.-J. Witkamp, R. Verpoorte, Y.H. Choi, Tailoring properties of natural deep eutectic solvents with water to facilitate their applications, Food Chem. 187 (2015) 14–19. doi:10.1016/J.FOODCHEM.2015.03.123.

[21] A. Paiva, R. Craveiro, I. Aroso, M. Martins, R.L. Reis, A.R.C. Duarte, Natural Deep Eutectic Solvents – Solvents for the 21st Century, ACS Sustain. Chem. Eng. 2 (2014) 1063–1071. doi:10.1021/sc500096j.

[22]   Y.H. Choi, J. van Spronsen, Y. Dai, M. Verberne, F. Hollmann, I.W.C.E. Arends, G.-J. Witkamp, R. Verpoorte, Are Natural Deep Eutectic Solvents the Missing Link in Understanding Cellular Metabolism and Physiology?, PLANT Physiol. 156 (2011) 1701–1705. doi:10.1104/pp.111.178426.

[23]   O. Gómez Rojas, I. Sudoh, T. Nakayama, S.R. Hall, The role of ionic liquids in the synthesis of the high-temperature superconductor $YBa_2Cu_3O_{7-\delta}$, CrystEngComm. (2018). doi:10.1039/C8CE01275J.

[24]   N. Doebelin, R. Kleeberg, Profex: A graphical user interface for the Rietveld refinement program BGMN, J. Appl. Crystallogr. 48 (2015) 1573–1580. doi:10.1107/S1600576715014685.

[25]   M.-Y. Chow, X.-M. Chen, T.C.W. Mak, Simultaneous binding of betaine and pseudohalide to cadmium: structures of four polymeric mixed-ligand cadmium(II) complexes, J. Chem. Soc. Dalt. Trans. 0 (1993) 3413. doi:10.1039/dt9930003413.

[26]   J. V. Quagliano, S. Kida, J. Fujita, Preparation and Infrared Studies of Metal Complexes Containing the Zwitterion Ligand Betaine , (CH) NCH COO, J. Am. Chem. Soc. 84 (1962) 724–729. doi:10.1021/ja00864a009.

[27]   B. Wang, L. Qin, T. Mu, Z. Xue, G. Gao, Are Ionic Liquids Chemically Stable?, Chem. Rev. 117 (2017) 7113–7131. doi:10.1021/acs.chemrev.6b00594.

[28]   A.P. Abbott, R.C. Harris, K.S. Ryder, C. D'Agostino, L.F. Gladden, M.D. Mantle, Glycerol eutectics as sustainable solvent systems, Green Chem. 13 (2011) 82–90. doi:10.1039/C0GC00395F.

[29]   A.P. Abbott, G. Capper, S. Gray, Design of Improved Deep Eutectic Solvents Using Hole Theory, ChemPhysChem. 7 (2006) 803–806. doi:10.1002/cphc.200500489.

[30]   S.A. Sunshine, T. Siegrist, L.F. Schneemeyer, D.W. Murphy, R.J. Cava, B. Batlogg, R.B. Van Dover, R.M. Fleming, S.H. Glarum, S. Nakahara, R. Farrow, J.J. Krajewski, S.M. Zahurak, J. V. Waszczak, J.H. Marshall, P. Marsh, L.W. Rupp, W.F. Peck, Structure and physical properties of single crystals of the 84-K superconductor Bi2.2Sr2Ca0.8Cu2O8+, Phys. Rev. B. 38 (1988) 893–896. doi:10.1103/PhysRevB.38.893.

[31]   M.A. Subramanian, C.C. Torardi, J.C. Calabrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry, A.W. Sleight, A New High-Temperature Superconductor: $Bi_2Sr_{3-x}Ca_xCu_2O_{8+y}$., Science. 239 (1988) 1015–7. doi:10.1126/science.239.4843.1015.
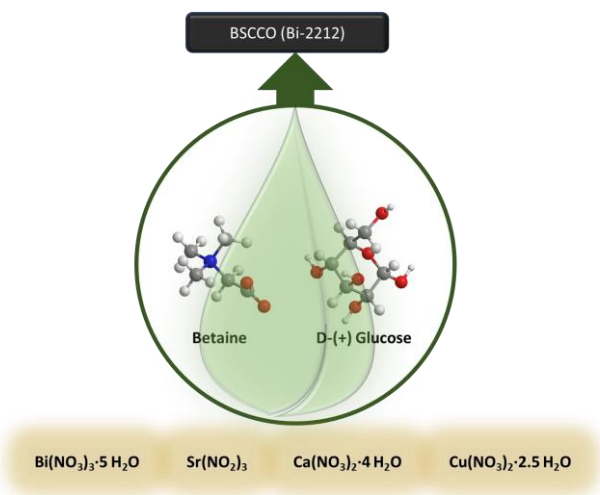
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Synopsis: This work presents for the first time the use of a natural deep eutectic solvent (NADES) for the synthesis of complex metal oxides such as Bi-2212 superconductor. 94 % of the superconductive phase was obtained upon calcination however, after 6 days it was observed a decay in percentage. Here we also present an analysis of the NADES stability based on aging process and how is affecting the overall outcome of synthetic procedure.