Asian Journal of Chemistry; Vol. 24, No. 9 (2012), 3879-3883

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Syntheses of Rubidium- and Cesium Triiodides in Supercritical Carbon Dioxide

K. XHAXHIU[1,*], A. MELE[1], A. MEMO[1], B. SEITI[1], T. KOTA[2] and K. DULE[3]

[1]Department of Chemistry, Faculty of Natural Sciences, University of Tirana, Tirana, Albania
[2]Department of Physics, Faculty of Natural Sciences, University of Tirana, Tirana, Albania
[3]Department of Mathematics, Faculty of Natural Sciences, University of Tirana, Tirana, Albania

*Corresponding author: Tel: +355 67 2547800; E-mail: kledi.xhaxhiu@unitir.edu.al

(*Received*: 29 September 2011; *Accepted*: 15 April 2012) AJC-11260

By knowing the physical-chemical properties of supercritical CO_2 and its extended use as an attractive continuous phase for different applications, we employed in this study supercritical CO_2 as a reaction medium for syntheses between inorganic species. In this course of investigation, aiming to obtain the ternary compounds M_2SnI_6 (M = Rb, Cs) in supercritical CO_2 using a self made lab-scale system at 200 ºC, 220 bar for one week, instead of the desired product, we obtained the triiodides of rubidium (RbI_3) and cesium (CsI_3). Small amounts of water, introduced as impurity played a determinant role in the syntheses, meanwhile, the presence of tin(IV) iodide and supercritical CO_2 were crucial factors for the occurrence of triiodides.

Key Words: Inorganic syntheses, Supercritical carbon dioxide, Triiodides of rubidium and cesium.

INTRODUCTION

Carbon dioxide (CO_2), due to its naturally occurrence and its abundant presence as a by-product of power plants and industrial plants and due to its favourable physical properties (T_c = 31.1 ºC; P_c = 73.87 bar) is becoming the most preferred supercritical fluid for different applications. One of its first applications in industry as a substitute of organic solvents is related to its extraction capacity of different natural products widely used in food, pharmaceutical and biotechnological industry[1-4]. For the consumer, the products extracted by supercritical CO_2 are more acceptable than if they were extracted by organic solvents. Further experiments on extraction using supercritical CO_2 presented that not only scents and oils could be extracted by this solvent but different elements, their oxides and salts could be extracted too. Using supercritical CO_2 and organic ligands, metal ions of earth alkali metals[5], transition metals[6], lanthanides and actinides[7] were successfully extracted. Nowadays this extraction method is seen as an alternative of purification of polluted soils from nuclear wastes, especially from uranium wastes[8]. Other applications qualify supercritical CO_2 as an alternative reaction medium for radical and ionic polymerizations[9,10], homogeneous and heterogeneous catalytic reactions[11,12]. Inspired from the properties and the extended applications of supercritical CO_2 in organic and polymer chemistry, inorganic chemists have employed it mainly as an effective reaction medium in different syntheses. Meanwhile this study aimed to test the dissolving capacity of supercritical CO_2 using it as a reaction medium in the reactions between inorganic species, such as Rb_2CO_3, Cs_2CO_3, SnI_4 and I_2. Although the goal of these reactions was the syntheses of the ternary compounds M_2SnI_6 (M = Rb, Cs), unexpectedly, these syntheses yielded the triiodides of rubidium and cesium respectively. Small amounts of water in the system caused the hydrolysis of tin (IV) iodide (SnI_4) yielding among other hydrogen iodide (HI) which reacted with the carbonates of rubidium and cesium leading the formation of the respective iodides. The latter being in a dense atmosphere of I_2/supercritical CO_2/H_2O fixed iodine forming though the triiodides. The role of water in these syntheses was fundamental and the presence of the tin(IV) was crucial. Its absence declined the reaction route of forming the triiodies. Instead only the iodides and iodates of rubidium and cesium were formed. By using a self made laboratory scale apparatus, were supercritical CO_2 served as a reaction medium inside the ampoule and as a counter-pressure agent outside the ampoule (inside the autoclave), we showed a new way of the syntheses of triiodides of rubidium and cesium different from the traditional one.

EXPERIMENTAL

The syntheses were carried out using the starting compounds: Cs_2CO_3 (powder 99.9 % purity), Rb_2CO_3 (powder 99.9 % purity) and iodine (crystals 99.9 % purity) delivered by ChemPur GmbH, Karlsruhe, Germany and SnI_4 (crystalline 95 % purity) by Alfa Aesar GmbH & Co KG, Karlsruhe, Germany. Carbon dioxide used in these reactions was obtained in form of a pressurized gas (99.999 % purity) in flasks, supplied by the company Messer Griesheim. GmbH, Germany.

Apparatus for the reactions in supercritical CO_2: A cylindrical batch reactor for periodical use was projected to carry out the synthesis in supercritical CO_2 (Fig. 1). It consisted of a stainless steel vessel with inner volume of 115 mL and a closing cork equipped with Viton-O-ring for tightening. Its upper limitation for regarding the working conditions: 400 bar and 400 ºC. Despite of it, these conditions could not be applied due to the properties of the Viton-O-rings, which tolerate temperatures up to 250 ºC. The proper use of this batch reactor required some auxiliary tools responsible for the indication of the reaction parameters and for the security of the system such as pressure gauge, overpressure valve and an outlet valve. These tools were joined to the autoclave cork by a steel capillary of 1.6 mm inner and 3.2 mm outer diameter. A direct contact of the starting compounds with the autoclave inner walls leads to undesired by-products, which not only deteriorate the intended synthesis but can also corrode the reactor and the measuring system. This difficulty is overridden by a similar preparation method described by Rabenau[13] for hydrothermal inorganic synthesis which uses quartz glass ampoules as reaction vessels and stainless steel autoclaves as vessels for counter-pressure environment.

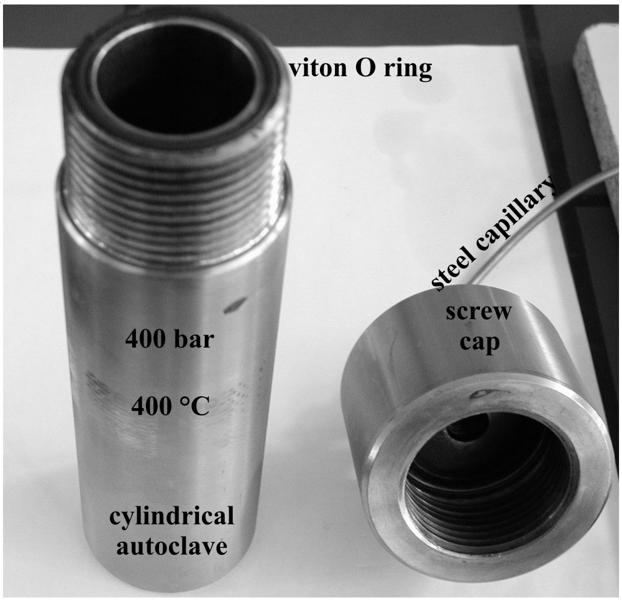

Fig. 1. Stainless steel cylindrical autoclave used for the reactions in supercritical CO_2

Primarily the stoichiometric weighted reactants were transferred into a quartz ampoule (Fig. 2), with 12 mm outer diameter and a narrowing at 11.5 cm from its bottom which facilitates the sealing process.

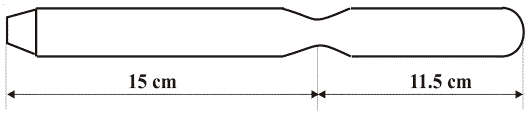

Fig. 2. A quartz ampoule used for the syntheses in supercritical CO_2. The narrowing close to its bottom facilitates its sealing in the H_2/O_2 flame

The quartz ampoule is attached further to the metering and supercritical CO_2-filling system consisting of six valves, two pressure outlets (described as air valves) and a glass flask (Fig. 3).

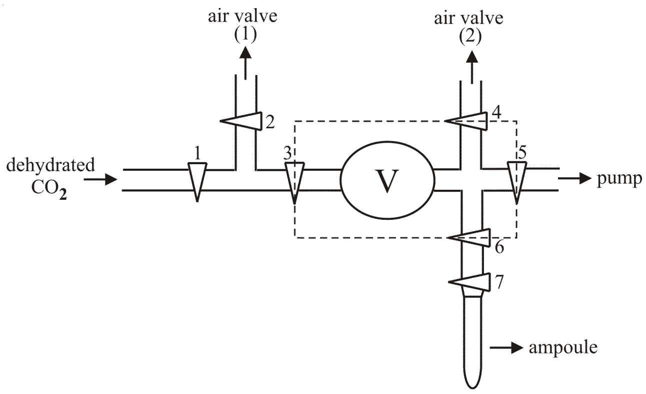

Fig. 3. Measuring and filling system. The confined region belongs to the defined volume of supercritical CO_2, which sublimates inside the ampoule

The valves serve as restrictors, keeping the defined amount of supercritical CO_2 inside the system, while the air valves provide a pressure equal to atmospheric pressure inside the system. The glass flask makes an important part of the system's volume. With its inner volume (V) contributes to total volume of 0.603 l confined by the valves 3, 4, 5, 6 (dashed-lines contoured region) corresponding to 1.095 g CO_2 at 293 K. The attached ampoule with the starting compounds in it was initially evacuated and then filled with defined amounts of dehydrated CO_2 using the metering and CO_2-filling system, while keeping its bottom permanently immersed in liquid nitrogen. The steps needed for the ampoule filling with the defined amounts of CO_2 are described in details elsewhere[14]. The sealed ampoule was preserved in liquid nitrogen until the necessary quantity of dry ice serving as counter-pressure agent was generated using the same system. Even though in principle it is possible to use water, argon or nitrogen as counter agents, the latter were not used due to the difference of their expansion coefficients compared to that of supercritical CO_2.

The weighed educts (0.5 g) were transferred into a quartz ampoule, which was evacuated, filled with supercritical CO_2 and sealed using H_2/O_2 flame. The sealed ampoule was placed inside the autoclave with the necessary amount of dry ice used as counter-pressure agent (to prevent the ampoule explosion). The autoclave was tighten and kept at ambient temperature for approx. 2 h. Then, it was placed in a dry oven and heated gradually (20 ºC/h) up to 200 ºC. The autoclave remained at this temperature generally for one week if no pressure diminution was observed. At these conditions the supercritical CO_2 inside and outside the ampoule (inside the autoclave) was in supercritical state. After one week, the system (Fig. 4) was cooled down to room temperature and gradually depressurized. Fast depressurization rates often led to abrupt ampoules explosions. The obtained sample (carefully separated from glass splitter if necessary) was ground and then investigated by electron microscopy and X-Ray diffraction measurements.

Characterization of the products: The determination of the samples morphology was performed with a CS44 SEM (Scanning Electron Microscope) delivered from the company

CamScan (Cambridge) equipped with a Robinson BSE (Back Scattering Electron) and SE (Secondary Electron) detector. Qualitative elemental analyses were carried out with the DS-710 144-10 EDX (Energy Dispersive X-ray Spectroscopy) system delivered from EDAX (Cambridge).

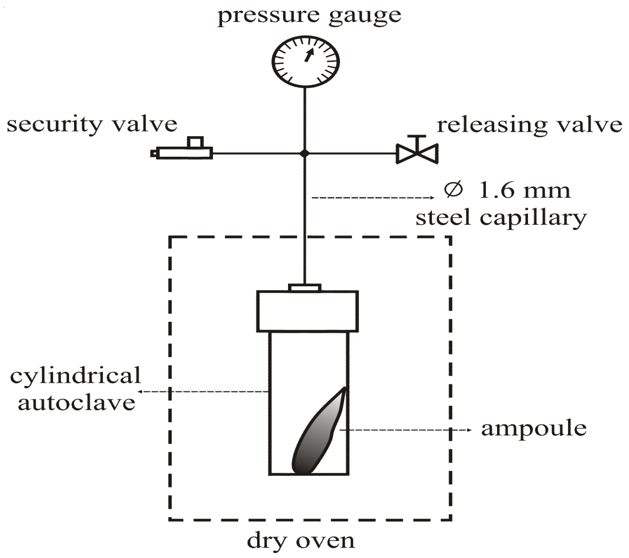

Fig. 4. A self made laboratory scale compact system for the reactions in supercritical CO_2

The X-Ray measurements were performed with a powder diffraction device D5000 delivered from SIEMENS (Karlsruhe) with CuK$_{\alpha 1}$-radiation (λ = 1.54051 Å) in transmission mode. The diffraction patterns were recorded by means of a Braun Position Sensitive Detector (PSD-50M) with an angular increment of 0.015° and a measuring time varying from 0.5-10 h.

RESULTS AND DISCUSSION

Using the self made laboratory scale apparatus described above, we aimed to synthesise the ternary compounds M_2SnI_6 (M = Rb, Cs) starting from the respective carbonates (as crystalline ionic compounds show poor solubility in supercritical CO_2) mixed with powdered tin(IV) iodide and iodine in stoichiometric amounts. This reaction was supposed to occur in supercritical CO_2 between dissolved tin(IV) iodide and iodine and the not dissolved carbonates. Tin(IV) iodide and iodine dissolve well in non polar organic solvents; therefore good solubility of them in supercritical CO_2 was expected as well. The latter was confirmed by our preliminary extraction experiments. The schematic of the intended reactions (1) was as following:

$M_2CO_3 + SnI_4 + I_2 \rightarrow M_2SnI_6$ + by-products (M = Rb, Cs) (1)

In order to perform them, in each case the autoclave (with the ampoule inside) was heated at 200 ºC and approx. 220 bars for one week. After one week, the system was slowly cooled down and depressurized. This process led always to the ampoule explosion inside the autoclave. For both reactions, the product was carefully extracted from the mixture of glass splitters. In both cases it consisted of dark-brown crystals mixed with an amorphous layer. The X-ray powder diffraction measurements recorded from each sample displayed the presence of triiodides of rubidium (RbI_3) and cesium (CsI_3) respectively (Figs. 5 and 6) instead of the expected ternary compounds. Although the aimed ternary compounds M_2SnI_6 (M = Rb, Cs) were not obtained, these syntheses awaked our interest, firstly because they presented a new way of obtaining the triiodides of rubidium and cesium differently from the traditional ones reported by Tebbe *et al.*[15] and Runsink *et al.*[16], which obtained them using the respective iodides and an iodine rich ethanolic solution. Secondly, in these syntheses, the substitution mechanism of the carbonate anions with the triiodide anions seemed to be of great interest.

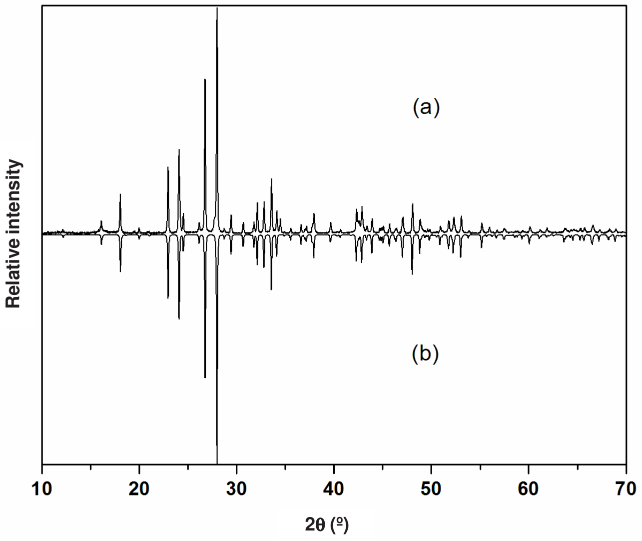

Fig. 5. X-ray diffraction patterns of rubidium triiodide (RbI_3). (a) the recorded powder pattern, (b) the calculated pattern from the ICSD data

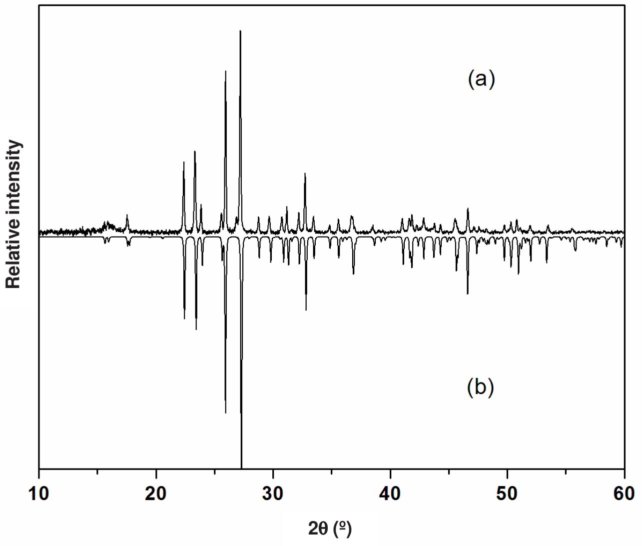

Fig. 6. X-ray diffraction patterns of cesium triiodide (CsI_3). (a) the recorded powder pattern, (b) the calculated pattern from the ICSD data

The direct substitution of carbonate ion with the triiodide ion just in the presence of supercritical CO_2 would sound somehow strange, due to the lower stability of it in comparison to the carbonate ion. Therefore to investigate the mechanism of these substitutions, we started to search the cause on other factors. Firstly, the sample purities were checked, performing DTA-TGA measurements of them.

The DTA-TGA measurements of the carbonate samples (Fig. 7(I), (II)) confirmed the presence of absorbed and crystalline water in the sample of rubidium carbonate (14.8 % w/w, Fig. 7 (I)) and mainly the presence of absorbed water in the sample of cesium carbonate [3.8 % w/w, Fig. 7 (II)]. Even though they were delivered with the reported purity, the later might result due to their long storage in the laboratory under ambient conditions. If this external factor would be considered for then, these amounts of water coming along with carbonates would cause a stepwise conversion of carbonates to iodides and iodates according to the reactions (2-4), but they cannot lead to the formation of triiodides.

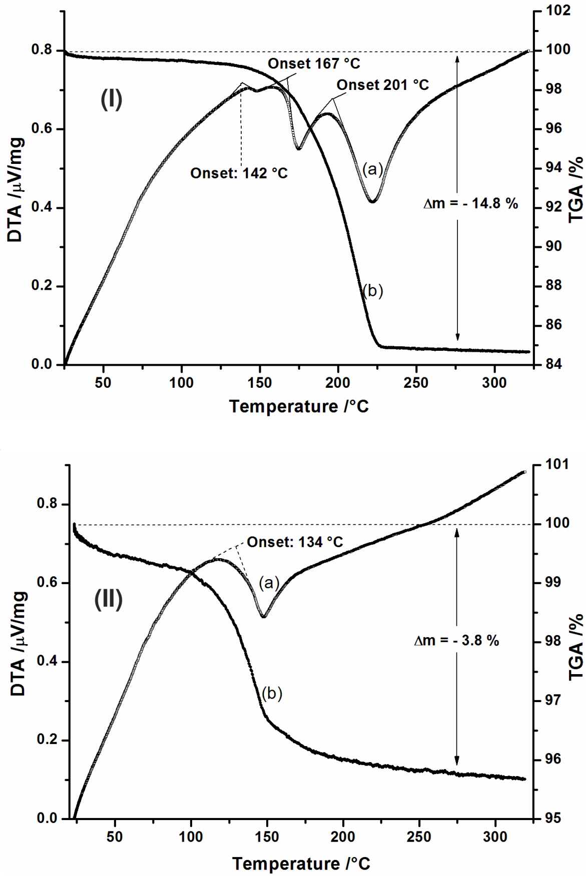

Fig. 7. Thermal measurements. (a) DTA, (b) TGA plots of (I) Rb_2CO_3 and (II) Cs_2CO_3

$$I_2 + H_2O \longrightarrow HI + HIO \quad (2)$$

$$3HIO \longrightarrow 2HI + HIO_3 \quad (3)$$

$$M_2CO_3 + HI + HIO_3 \longrightarrow MI + MIO_3 + CO_2 + H_2O \quad (4)$$

The presence of these amounts of water coming along with carbonates can cause a stepwise conversion of carbonates to iodides and iodates but it cannot lead to the formation of triiodides by this mechanism. Closer observation of the powder patterns of triiodides of rubidium and cesium does not show reflections belonging to iodides and iodates (according to the above mechanism). Rather noticeable in both the powder patterns of Figs. 5 and 6 is the absence of the reflections of tin(IV) iodide or its related compounds, in case it is involved in any reaction. As mentioned above, it was transferred in stoichiometric amounts into the ampoule in the powdered form along with other starting compounds. Further detailed investigations using electron microscopic techniques such as EDX (Fig. 8) and SEM (Fig. 9) of the bulk products of both samples were recorded.

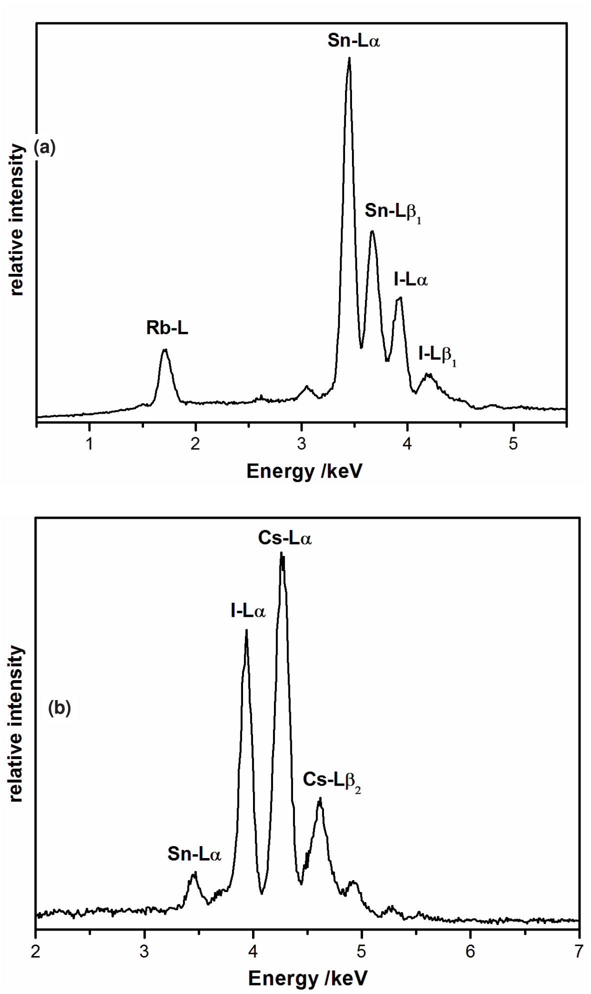

Fig. 8. EDX spectra of dark brown products obtained from the reaction: (a) $Rb_2CO_3 + SnI_4 + I_2$, (b) $Cs_2CO_3 + SnI_4 + I_2$

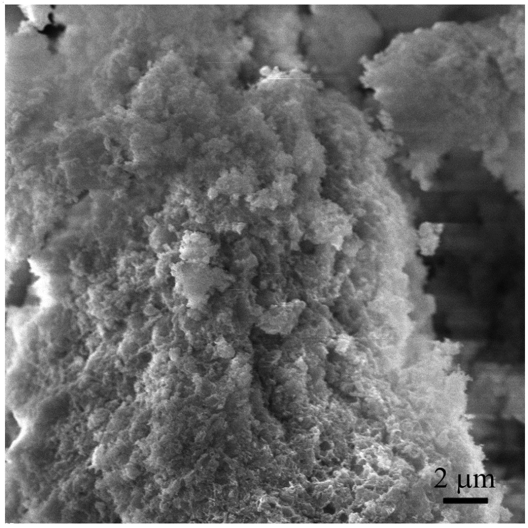

Fig. 9. SEM image of the dark brown product obtained from the reaction: $Rb_2CO_3 + SnI_4 + I_2$

The SEM image recorded from the bulk products (Fig. 9) displayed the presence of amorphous materials interweaving the product, while the corresponding EDX spectra (Fig. 8) showed the presence of tin in it. Therefore, it is assumed that the presence of water in the system has caused the hydrolysis of tin(IV) iodide (water sensitive) to tin hydroxide (amorphous) and hydrogen iodide, according to the reaction (5).

$$SnI_4 + 4H_2O \rightarrow Sn(OH)_4 + 4HI \qquad (5)$$

At such conditions small amounts of water are mixed with supercritical CO_2 and the water plays the role of the co-solvent. Once hydrogen iodide is released by the reaction (5), it reacts with the carbonates yielding the respective metal iodides as follows:

$$M_2CO_3 + 2HI \rightarrow 2MI + CO_2 + H_2O \qquad (6)$$

The metal iodides being in contact to the dense $I_2/H_2O/$ supercritical CO_2 atmosphere, which is similar to the saturated iodine alcoholic solution, yielded the respective triiodides. The overpressure inside the ampoule created by the released CO_2 as showed by the reaction (6) was compensated by a higher amount of dry ice (solid CO_2) used as counter pressure agent. The quartz ampoules could resist a pressure difference outside-inside of 30 bar.

In order to confirm the role of tin(IV) iodide in the formation of triiodides, a comparative experiment, applying the same conditions and using the same system, involving only rubidium carbonate and iodine was carried out. The products of it were merely rubidium iodide and rubidium iodate (Fig. 10). In this case, the water/supercritical CO_2 mixture favours reactions (2), (3) and (4). No traces of triiodides were observed. Confirming so the necessity of the presence of tin(IV) iodide for the syntheses of triiodides.

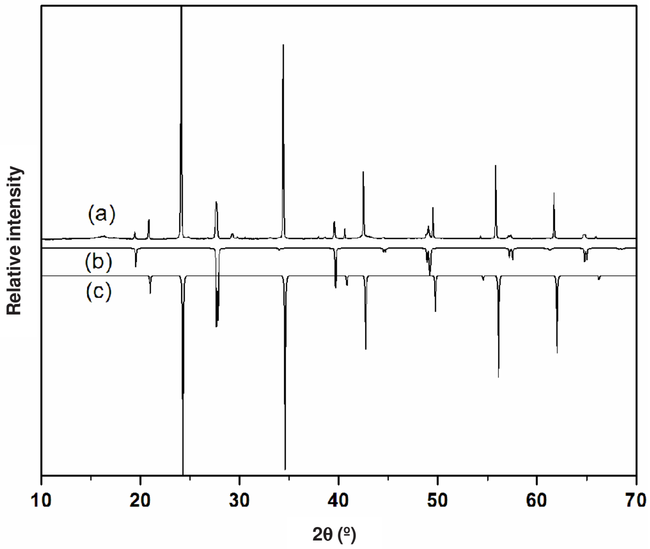

Fig. 10. Diffraction patterns of (a) measured powder sample from the reaction $Rb_2CO_3 + I_2$ in supercritical CO_2, (b) calculated pattern of rubidium iodate from the ICSD data, (c) calculated pattern of rubidium iodide from the ICSD data

Conclusion

In this study a self-made laboratory system was used for the reactions of inorganic species in supercritical carbon dioxide. The latter is considered firstly as a medium (environment) for the reactions occurring between carbonates of rubidium, cesium and tin(IV) iodide in the presence of crystalline iodine and secondly as a counter pressure agent in order to prevent the quartz ampoule explosion. Even though that the syntheses of the ternary compounds M_2SnI_6 (M = K, Rb, Cs) were aimed in each case, the reactions occurring between the above species yielded the triiodides of rubidium and cesium when the respective carbonates were used. The presence of water as impurity in all the employed carbonates was a determinant factor for the syntheses occurrence. However, tin(IV) iodide (SnI_4) played a crucial role in the formation of the triiodides of rubidium (RbI_3) and cesium (CsI_3). Its hydrolysis in the presence of water yielded the hydroiodic acid (HI) which served as a precursor for the formation of the iodides of rubidium (RbI) and cesium (CsI) respectively. The latter being in a dense atmosphere of iodine dissolved in supercritical CO_2 led to the formation of triiodides. Comparative syntheses without the presence of tin(IV) iodide did not yield the respective triiodides, instead of them, the formation of iodides and iodates of rubidium and cesium occurred. In spite of this, these syntheses shed light to a new method for the preparation of triiodides of rubidium and cesium in a green solvent such as supercritical CO_2.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the financial support of the German Research Foundation (DFG) and the University of Siegen. Special thanks are dedicated to the group leader of Inorganic and Solid State Chemistry University of Siegen, Prof. Dr. H.-J. Deiseroth for his keen interest and active support for the realization this work and to Dr. C. Rainer for his generous help with the SEM and EDX analysis.

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