Materials Research Express

PAPER

Substitution of Ca$^{2+}$ by Sn$^{2+}$ and Sr$^{2+}$ cations in \emph{P. placenta} shells and single-crystal calcite through ion exchange reactions

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Keywords: perovskite synthesis, calcite, strontianite, ion exchange

Abstract

Tin (Sn$^{2+}$) and strontium (Sr$^{2+}$) are potential replacements to lead (Pb$^{2+}$) in perovskite synthesis since Sn is on the same IVA group in the periodic table as Pb while Sr is a promising alternative according to Goldschmidt’s rules and quantum mechanical analysis. The crystal radii of their ions are also nearly identical with Pb$^{2+}$ = 1.33 Å, Sn$^{2+}$ = 1.36 Å, and Sr$^{2+}$ = 1.32 Å. In this study, both Sn and Sr were explored in transforming calcite, a polymorph of calcium carbonate (CaCO$_3$) into a leaching group in the first step of a sequential ion-exchange reaction towards perovskite formation. Instead of forming the intermediate tin carbonate (SnCO$_3$), the reaction resulted in the formation of gypsum or calcium sulfate dihydrate (CaSO$_4$·2H$_2$O) and Sn in the form of oxides. These oxides, however, are useful especially when these are in the form of tin dioxide-coated CaCO$_3$ shell-core structures—having demonstrated flame retardant and smoke suppressant properties. On the other hand, calcite was successfully transformed into strontium carbonate (SrCO$_3$) or strontianite through the cation exchange reaction. X-ray diffraction (XRD) and X-ray Photoelectron Spectroscopy (XPS) were used to observe the resulting materials and understand the transformation of both \emph{Placuna placenta} (or Capiz) shells and single-crystal calcite from the ion-exchange reactions.

1. Introduction

The synthesis of perovskite materials has gone beyond the traditional solution processing techniques. There are other methods now that can produce perovskite materials in either thin film [1] or bulk form [2]. One such route is through a sequential ion exchange that transforms carbonate materials into perovskites. The advantages of this route include its simplicity as a two-step reaction scheme for converting carbonate architectures into halide perovskites. This process is also carried out at room temperature only with the resulting materials typically inheriting the 3D shape, fine features, and crystallinity of the starting materials. The use of Pb, the most successful element in terms of perovskite solar cell (PSC) efficiency performance, was already successfully demonstrated in an ion exchange process in transforming calcite to cerussite [3] and into a perovskite material [4]. The issue of Pb’s toxicity, however, continues to hinder its use, and it has become one of the major stumbling blocks in its commercialization [5]. Other Pb-free alternatives such as Sn and Sr are also open for exploration to validate the feasibility of using the same ion exchange routes in the first step of transforming calcite into Pb-free perovskite materials.

In this work, Sn was chosen since it has the most potential to replace Pb since both are on the same IVA group in the periodic table and for the similarity in crystal radii of their ions (Pb$^{2+}$, Sn$^{2+}$) at 1.33 and 1.36 Å, respectively [6]. It is also the most successful replacement element for Pb so far for PSCs [7, 8]. Methylammonium tin triiodide (MASnI$_3$) has a lower bandgap (1.2 to 1.4 eV) that induces a broader absorption spectrum as compared with the benchmark MAPbI$_3$ counterpart (1.6 eV) [9]. Aside from the potential PSC application for Sn through this route, it is also of interest to explore tin dioxide-coated CaCO$_3$ shell-core structures for materials with the potential to demonstrate flame retardant and smoke suppressant properties [10]. On the other hand, Sr is non-toxic and relatively inexpensive. Strontium is a divalent cation that is located

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in the same column of the periodic table of the elements as Ca, and with similar chemical properties and interactions—enabling the replacement of Ca by Sr in biomineralization processes. Strontium is also regarded as one of the most promising alternatives according to Goldschmidt's rules and quantum mechanical analysis [11, 12]. Goldschmidt's rules are based on empirical observations of ion replacement in natural minerals while keeping the crystal structure more or less unchanged. These rules apply to a class of compounds with the general formula ABX³ that crystallizes in a perovskite structure. Here, A and B are two different cations, and X is an anion binding the two cations together. The first rule states that an element can extensively replace those of another in ionic crystals if their radii differ by less than 15%. The crystal radius of Sr²⁺ (1.32 Å) and Pb²⁺ (1.33 Å) are nearly identical [6] with a difference of only 0.75%, implying that the substitution won't greatly affect the crystal structure. Another indicator for the stability and distortion of crystal structures is Goldschmidt's tolerance factor, t which is computed based on the crystal radii of A, B, and X ions. Using the crystal radii of CH₃NH₃ and I, the value of t in using Pb²⁺ and Sr²⁺ cations are 0.805 and 0.807, respectively. For a t value between 0.7 and 0.9, the A ion is too small, or the B ion is too large, for a cubic structure. The t values for Pb²⁺ and Sr²⁺ are consistent with a noncubic perovskite structure that could either be orthorhombic, rhombohedral, or tetragonal structure. Quantum mechanical theory, on the other hand, comes into play when not only the crystal radii of the ions are considered but also the electrostatic potential between the atoms and the difference in electronegativity of the elements involved.

The bandgap for MASrI₃ was estimated at 3.6 eV from a Density Functional Theory (DFT) simulation [11]. It is considerably higher than that for the lead perovskite and, therefore, not suitable for direct solar cell applications but can be used as a charge-selective contact material and as a top cell in tandem architectures. It is important to note that aside from the potential PSC application for Sr being incorporated in calcite, Sr as a trace element in CaCO₃ had been used as an indicator of the Earth’s past climate conditions [13] and had provided a basis for dating marine carbonate, evaporite and phosphate samples [14].

Cation exchange was already successfully carried out for Sr⁵⁺ in transforming calcite to strontianite [15] while it was not the case for Sn⁴⁺. From the start of the study, it was already known that tin as carbonate is not a stable compound and it is not listed as one of the carbonates. It also lacks important information such as XRD and x-ray absorption spectroscopy (XAS) spectra in literature. Sn’s success as a substitute element to Pb in perovskites research prompted its inclusion in this study. Tin (II) sulfate was chosen as a source of Sn⁴⁺ as it is a convenient source of tin (II) ions uncontaminated by tin (IV) species. However, as there are two main oxidation states, +2 and the slightly more stable +4, with the +2 easily oxidized by atmospheric oxygen, its formation is not guaranteed. A +2-oxidation state is important in this case as it is also the oxidation state for Ca⁴⁺ in calcite. Sr²⁺, unlike Sn⁴⁺, is available as a nitrate—something that is highly soluble in water and also has an oxidation state of +2. The use of nitrate in solutions facilitates successful reactions due to its solubility. On the other hand, the use of sulfate may result in another sulfate formation in the form of Ca⁵⁺. Comparing the crystal radii of the two, Sn²⁺’s radius is 1.36 Å while that of Sr²⁺ is 1.32 Å, much smaller and much nearer to that of Pb²⁺ (1.33 Å). It should also be noted that the Sn⁷⁺ coordination number (CN) for this radius is 7 while for Ca²⁺, Pb²⁺, and Sr²⁺, CN is 6 [6]. For a successful ion exchange, the ionic radius should be smaller for the outgoing cation, in this case, Ca²⁺ (1.14 Å) than the incoming cation—Pb²⁺, Sn²⁺, or Sr²⁺ [16].

2. Materials and methods

2.1. Materials

P. placenta (or Capiz) shells ≈ 3 to 5 cm diameter were from Oton, Iloilo, Philippines, single-crystal CaCO₃ (100) orientation, 10 × 10 × 0.5 mm, one side polished and single-crystal CaCO₃ (001) orientation, 10 × 10 × 0.5 mm, 2-side polished (MTI) (figure 1), Tin (II) sulfate ≥95% and Strontium nitrate ACS reagent ≥99% (both from Sigma Aldrich).

2.2. Methodology

2.2.1. Preparation of the P. placenta shells

Seven pieces of shells were cleaned by immersing them in acetone for 1 h and in deionized water for another hour. These were then bleached in 0.5 M potassium hydroxide (KOH) in a deionized water solution for seven days. The shells were immersed in deionized water for 24 h to remove the remaining KOH. The shells were dried at ambient temperature for another 24 h.

2.2.2. CaCO₃ to SrCO₃/SrCO₃ Conversion (P. placenta shell strips/powder in SnSO₄/Sr(NO₃)₂ solutions)

150 ml deionized water was degassed by bubbling nitrogen through it for 1 h. SnSO₄ and Sr(NO₃)₂ powders were separately dissolved at 0.5 M and 1 M concentrations in degassed, deionized water on a magnetic stirrer while a continuous flow of nitrogen was applied. The shells were cut into strips 0.75 cm by width and immersed in...
acetone for 1 h and allowed to air dry for 15 min. The samples (1 gram each) were immersed in separate 10 ml SnSO₄ and Sr(NO₃)₂ solutions. The setup was kept oxygen-free. After immersion, the shells were soaked in deionized water for 24 h. The shells were then washed with deionized water, immersed in acetone for 1 h, and allowed to air dry for 30 min. The experiments were varied in terms of 1. concentration (0.5 M and 1 M), 2. pressure (low pressure or LP (immersion time: 4 h low pressure/20 h atmospheric pressure), and atmospheric pressure or AP (immersion time: 24 h atmospheric pressure)), and 3. sample form (powder, P and shell strips, S).

2.2.3. CaCO₃ to SnCO₃/SrCO₃ Conversion (Single crystal calcite)
Single crystal calcite with (100) and (001) orientations was cleaved into 4 to 5 irregular shapes and placed on scintillation bottles with the polished surface facing up. Each bottle was filled with 20 ml of either SnSO₄ or Sr(NO₃)₂ solutions at 0.5 M concentration. Separate samples for each solution were immersed for 8, 16 and 24 h at atmospheric pressure and room temperature (30 °C) with the bottles capped loosely. The crystals were immersed in deionized water for 24 h to stop the conversion reaction, washed with deionized water, immersed in acetone for 1 h, and allowed to air dry for 30 min.

3. Experimental methods
Powder XRD measurements were performed using Shimadzu Maxima XRD-7000 x-ray diffractometer with Cu radiation at 40 kV and 30 mA at a scan speed of 3 deg min⁻¹. The XPS beamline uses a PHI5000 Versa probe II (ULVAC-PHI, Japan) equipped with a hemispherical electron energy analyzer. The excitation source is a monochromatic Al Kα x-ray gun (1,486.6 eV). The binding energy of all XPS spectra was calibrated with the C1s peak at 284.8 eV.

4. Results and discussion
4.1. Sn²⁺ → Ca²⁺ Cation Exchange in P. placenta Shells
Below equation (1) shows the expected transformation of CaCO₃ immersed in a tin sulfate (SnSO₄) solution to form tin carbonate:

\[ SnSO_4(aq) + CaCO_3(s) \leftrightarrow SnCO_3(s) + CaSO_4(aq) \]  

The hexagonal calcite is the most thermodynamically stable crystalline phase of CaCO₃ as compared with the other two polymorphs: aragonite and vaterite [17]. Figure 2 shows the XRD pattern of calcite [18] as compared with those of the 4 samples that underwent cation exchange at different conditions. The peaks that characterize calcite at 2θ are 23.1, 31.4, 36, 39.4, 43.2, 47.5, and 48.5°, with the highest peak at 29.4° indexed at (104). In the patterns of the 4 Sn → Ca exchange samples however, new phases manifest as observed at values of 11.6, 20.7, and 26.9°, which are characteristic peaks of gypsum [19]. Instead of forming SnCO₃, the cation exchange resulted in gypsum (CaSO₄·2H₂O or CaH₄O₆S) in solid form.

From the XRD patterns using Match! [20], the LP samples showed higher gypsum peaks (or faster reaction rate) as compared to the AP sample. The patterns also show a more rapid reaction rate in higher concentration (1 M) as compared to a lower concentration (0.5 M) solution. It was also demonstrated that the powdered shell was converted faster than the shell strips. The gypsum phase increased from 5.6 to 66% while that of calcite decreased from 78.4 to 29% after ion exchange on these conditions. However, the XRD pattern quantification showed no SnCO₃ phase. Since XRD information on this compound is not available, further analyses were done.
There were other crystalline phases found based on Match! namely, the tetragonal tin oxide (SnO) with 2θ peaks at 37, 50.5 and 57.2° and the rutile tetragonal tin dioxide (SnO₂) with 2θ peaks at 33.6, 37.7, and 51.5° as referenced from published XRD data [21]. XRD patterns also showed that there was no undissolved or precipitated tin sulfate (SnSO₄), the reagent used in the experiments.

4.2. Sr²⁺ → Ca²⁺ cation exchange in P. placenta shells
The Sr samples still showed a predominantly calcite pattern. However, the patterns also contain 2θ peaks at 25.3, 26, 36.8, 44.3, and 50.1°, which are characteristic peaks of strontianite (SrCO₃) [22], as seen in figure 3. Below equation (2) shows the expected calcite to strontianite transformation:

$$ \text{Sr(NO₃)}₂(\text{aq}) + \text{CaCO}_₃(s) \leftrightarrow \text{SrCO}_₃(s) + \text{Ca(NO₃)}₂(\text{aq}) $$

From Match! [20], similar to the case of Sn, it can be observed that the transformation to strontianite increased from 6.5 to 30.8% for the four samples that underwent ion exchange at different conditions. Likewise, the samples showed a decrease in the calcite phase from 93 to 68.1%. LP samples also showed higher strontianite peaks than that of the AP sample. Again, this confirms that cation exchange at low pressure contributes to a faster reaction rate. The patterns also show a more rapid reaction rate in a higher concentration (1 M) as compared to a lower concentration (0.5 M). It is also demonstrated that the powdered shell was converted faster than the shell strips. Unlike Sn, Sr is known to form into carbonate, with known material properties and XRD pattern as the mineral strontianite.
4.3. Sn\(^{2+}\) → Ca\(^{2+}\) cation exchange on single-crystal calcite

Ion exchange is the solution chemistry route while diffusion is the resulting mechanism on the surfaces of the calcite materials investigated. A part of this study aims to investigate Sn\(^{2+}\) and Sr\(^{2+}\) cations as these are exchanged with the Ca\(^{2+}\) cation in calcite at 0.5 M concentration, atmospheric pressure, and room temperature solution. To detect the presence of these elements, XPS was used to analyze the surface chemistry in terms of Sn and Sr presence on the surface of the resulting materials. For both Sn and Sr, three samples of the same solution were subjected to immersion times of 8, 16, and 24 h while a 4th sample has a 24 h immersion time.

Based on the XPS results in figure 4, the atomic concentration of the incoming cation Sn\(^{2+}\) increases with increasing immersion time—from 8 (a) to 16 (b) and 24 h (c). This increase, shown in terms of the peak intensities of 3d\(_{5/2}\) and 3d\(_{3/2}\), is indicative of the rise in the number of cations exchanged as a function of time. The standard XPS spectra of Sn for 3d\(_{5/2}\) is 485 eV and 3d\(_{3/2}\) = 493.41 eV with Δ = 8.41 [23]. Comparing 24h\(_{100}\) (c) and 24h\(_{001}\) (d), it can be observed that (c) has higher 3d\(_{5/2}\) and 3d\(_{3/2}\) peaks as compared to (d). This was explained by a previous study [15] where wider spaces available for Ca\(^{2+}\) cations in (100) orientation allow for higher cation exchange rate while the Ca\(^{2+}\) cations are adjacent to each other in (001) orientation—restricting movement for incoming cations. From the same standard XPS spectra reference [23], the binding energies of SnO for 3d\(_{5/2}\) is from 486 to 486.8 eV while for SnO\(_2\), it is 486.4 to 486.9 eV. The results from figure 4 show that 16h\(_{100}\) (b) and 24h\(_{001}\) (d) align with the binding energy of SnO while that of 24h\(_{100}\) (c) to the binding energy of SnO\(_2\). The binding energy of 8 h\(_{100}\) (a) on the other hand, falls within the range of both SnO and SnO\(_2\). These results mean that the oxides of Sn present in the samples under XPS were predominantly SnO.

From XRD, it was shown that gypsum was formed instead of Sn as a carbonate. The presence of phases of Sn as oxides in XRD is also supported by the XPS results [15] showing that Sn\(^{2+}\) was formed mostly in the form of oxides, with small amounts of Sn as metal. This was also confirmed by XAS from the same study which was used to determine the local environment of Sn in the cation exchange-treated single-crystal calcite. The Sn sample analyzed was found to be more similar to SnO than SnO\(_2\) and, therefore, leans to an oxidation state of 2+ instead of 4+.

Although the Sn oxide content cannot be further broken down into SnO and SnO\(_2\) oxides in XPS, the results confirm the XRD and XAS findings on the presence of these oxides, with both techniques showing the more dominant presence of SnO as compared to SnO\(_2\). The results from XRD, XAS, and XPS reveal the formation of oxides of Sn—SnO, and SnO\(_2\) instead of SnCO\(_3\). The two carbonates (Sn\(^{2+}\) and Sn\(^{4+}\)) tend to decompose releasing CO\(_2\) either during synthesis or when heated and as such, are considered as oxides of their relevant cations, rather than containing the CO\(_3\) anion [24]. SnCO\(_3\) tends to decompose to SnO while Sn(CO\(_3\))\(_2\)—to SnO\(_2\). The release of CO\(_2\) in gas form makes this possible as illustrated by equation (3) below:
SnSO\textsubscript{4}(aq) + CaCO\textsubscript{3}(s) \leftrightarrow SnO(s) + CaSO\textsubscript{4}(s) + CO\textsubscript{2}(g)  \tag{3}

As no heat was involved with SnSO\textsubscript{4} in solution chemistry, the decomposition of SnCO\textsubscript{3} accompanied by the release of CO\textsubscript{2} can be attributed to the reactions from the synthesis. The formation of oxides of Sn instead of SnCO\textsubscript{3} after an ion exchange process using CaCO\textsubscript{3} as starting material, however, has its advantages. In a study \cite{10}, a semirigid polyvinyl chloride (PVC) treated with a SnO\textsubscript{2}-coated CaCO\textsubscript{3} had shown better flame retardant and smoke suppressant properties as compared to the same PVC treated with stand-alone CaCO\textsubscript{3}, SnO\textsubscript{2}, and a mixture of CaCO\textsubscript{3}/SnO\textsubscript{2}. The findings were based on the results of the limiting oxygen index, char yield, and smoke density rating (SDR) methods. These results indicate the possibility of core/shell structures of CaCO\textsubscript{3}/SnO\textsubscript{2} in similar applications.

4.4. Sr\textsuperscript{2+} → Ca\textsuperscript{2+} cation exchange on single-crystal calcite

For the Sr XPS results as shown in figure 5, the atomic concentration of the incoming cation Sr\textsuperscript{2+} also increases with increasing immersion time—from 8 (a) to 16 (b) and 24h (c), similar to that of Sn\textsuperscript{2+}. This increase, shown in terms of the peak intensities of 3d\textsubscript{5/2} and 3d\textsubscript{3/2} is also indicative of the rise in the number of cations exchanged as a function of time. The standard XPS spectrum of Sr for 3d\textsubscript{5/2} = 134.3 eV and 3d\textsubscript{3/2} = 136.09 eV with \( \Delta = 1.79 \) \cite{23}. The spectra for 8 h (a) and 16 h (b) appear similar and the peaks are not as prominent as 24 h (c) but it can be noted that 16 h (b) has moved towards a standard Sr XPS spectrum due to its \( \Delta = 2.08 \), closer to the standard \( \Delta = 1.79 \), as compared to 8 h (a)’s \( \Delta = 5.1 \). Comparing 24h\textsubscript{(100)} (c) and 24h\textsubscript{(001)} (d), it can be observed that (c) has higher 3d\textsubscript{5/2} and 3d\textsubscript{3/2} peaks as compared to (d). The same explanation applies as discussed in the case of Sn. The results from figure 5 show that all samples: 8h\textsubscript{(100)} (a), 16h\textsubscript{(100)} (b), 24h\textsubscript{(100)} (c), and 24h\textsubscript{(001)} (d) have binding energies closest to that of SrCO\textsubscript{3} as compared the binding energies of other compound types such as pure Sr and SrO. From the same reference \cite{23}, the binding energy of SrCO\textsubscript{3} for 3d\textsubscript{5/2} ranges from 133.1 to 133.6 eV.

Strontianite formation shown in XRD is supported by the XPS results showing that the composition of Sr3d is mostly SrCO\textsubscript{3}. The absence of doublet typical in calcite or Sr in calcite in the XAS results \cite{15} showed that the local structure of Sr in the sample is in the carbonate structure of SrCO\textsubscript{3} and not calcite nor Sr in calcite. XRD, XAS, and XPS results have confirmed the formation of SrCO\textsubscript{3} or strontianite.

5. Conclusions

The substitution of Ca by Sn and Sr in calcite follows the concepts of diffusion as it was experimentally shown that a cation exchange reaction is faster at low pressure versus atmospheric pressure, at high versus low concentration, and with porous (powdered) versus solid (strips) shells. Calcite to strontianite transformation

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure5.png}
\caption{Element specific XPS narrow scan spectra for Sr3d at different immersion times: (a) 8 h, (b) 16 h and (c) 24 h at (100) orientation. The spectrum of 24 h\textsubscript{(100)} is then compared with another Sr sample processed at the same 24h immersion time but of a (d)\textsubscript{(001)} orientation.}
\end{figure}
was confirmed by both XRD and XPS. Instead of forming SnCO₃, the cation exchange resulted in gypsum (CaSO₄) formation in solid form and Sn in the form of oxides. The results reveal the formation of oxides of Sn—SnO, and SnO₂ instead of SnCO₃. SnCO₃ tends to decompose to SnO while Sn(CO₃)₂—SnO₂ due to the release of CO₂ during synthesis. For this reason, oxides are formed out of the relevant cation Sn, rather than containing the CO₃ anion. Sn and Sr diffusion into calcite was also confirmed by XPS. The atomic concentration for both the incoming cations (Sn²⁺ and Sr²⁺) increased with increasing immersion time as shown by the peak intensities. The Sn oxides were found to be more of SnO than SnO₂ based on both XRD and XPS results. The wider ionic spacing of Ca²⁺ in calcite for (100) orientation accounts for the higher XPS peak intensities for both Sn and Sr as compared to (001) orientation.

Acknowledgments

This work was funded by a grant under the Engineering Research and Development for Technology (ERDT) of the Department of Science and Technology (DOST), Republic of the Philippines. The XRD characterizations were performed under a joint project of the Institute of Chemistry (IC) and National Institute of Geological Sciences (NIGS) of the College of Science, University of the Philippines-Diliman, Quezon City, Philippines. The XPS characterizations were made possible under beamtime application ID # 5855: BL5.3 SLRI X-ray Photoelectron Spectroscopy (XPS) performed at the Synchrotron Light Research Institute (SLRI), Nakhon Ratchasima, Thailand.

6. Conflicts of interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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References

[1] Sheng R, Ho-Baillie A, Huang S, Chen S, Wen X, Hao X and Green M A 2015 J. Phys. Chem. C 119 3545
[2] Dang Y, Liu Y, Sun Y, Yuan D, Liu X, Lu W, Liu G, Xia H and Tao X 2015 Cryst. Eng. Comm. 17 665
[3] Yuan K, Lee S S, De Andrade V, Sturchio N C and Fenter P 2016 Environ. Sci. Technol. 50 12984
[4] Holts T, Helmbrecht L, Hendrikse H C, Baglia I, Meuret S, Adhikaraka G W, Garnett E C and Noorduin W L 2018 Nat. Chem. 10 740
[5] Zhang Q, Hao F, Li J, Zhou Y, Wei Y and Lin H 2018 STAM 19 425
[6] Shannon R D 1976 Acta Cryst. A 32 751
[7] Liu C, Li W, Fan J and Mai Y 2018 J Energy Chem 27 1054
[8] Zhang Q, Ting H, Wei S, Huang D, Wu C, Sun W, Qu B, Wang S, Chen Z and Xiao L 2018 Mater. Today Energy 8 157
[9] Konstantakou M and Stergiopoulou T 2017 J. Mater. Chem. A 5 11518
[10] Xu J, Jiao Y, Zhang B, Qu H and Yang G 2006 J. Appl. Polym. Sci. 101 731
[11] Jacobsson T J, Pazoki M, Hagfeldt A and Edvinsson T 2015 J. Phys. Chem. C 119 25673
[12] Pazoki M, Jacobsson T J, Hagfeldt A, Boschloo G and Edvinsson T 2016 Phys. Rev. B 93 144105
[13] Gaetani G A and Cohen A L 2006 Geochim. Cosmochim. Acta. 70 4617
[14] Burke W H, Denison R E, Hetherington E A, Koepnick R B, Nelson H F and Otto J B 1982 Geology 10 516
[15] Junio J B, Chirawatkul P, Conato M T and Mercado C C. 2021 J. Phys. Chem. C 119 25673
[16] Rivest J B and Jain P K 2013 Environ. Sci. Technol. 47 8299
[17] Sarkar A and Mahapatra S 2010 Cryst. Growth Des. 10 2129
[18] Xu B and Poduska K M 2014 Phys. Chem. Chem. Phys. 16 17634
[19] Lopez-Delgado A, Lopez-Andres S, Padilla I, Alvarez M, Galindo R and Vazquez A J 2014 Geomat. Asia 4 82
[20] Putz H and Brandenburg K Match!- Phase Analysis using Powder Diffraction, Crystal Impact GmbH, Kreuzherrenstr. 102, 53227 Bonn, Germany, [https://crystalimpact.de/match]
[21] Hadia N, Ryabtsev S, Iomnashevskaya E and Seredin P 2009 Condens. Matter Interfaces 11 5
[22] Qian W Y, Sun D M, Zhu R R, Du X L, Liu H and Wang S L 2012 Int. J. Nanomedicine 7 5781
[23] Moulder J F, Stickle W F, Parrish K D and Bomben K D 1992 Handbook of X-ray Photoelectron Spectroscopy (Minnesota: Perkin-Elmer Corporation)) p 104 126
[24] Holdsworth A F, Horrocks A R and Kandola B K 2017 Polym. Degrad. Stab. 144 420