



Solvothermal and mechanochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$ enabled by the redox reactivity of $(\text{S}^{2-})_2$ pairs

Shunsuke Sasaki, Gwladys Steciuk, Catherine Guillot-Deudon, Maria Teresa Caldes, Isabelle Braems, Etienne Janod, Benoît Corraze, Stéphane Jobic, Laurent Cario

► To cite this version:

Shunsuke Sasaki, Gwladys Steciuk, Catherine Guillot-Deudon, Maria Teresa Caldes, Isabelle Braems, et al.. Solvothermal and mechanochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$ enabled by the redox reactivity of $(\text{S}^{2-})_2$ pairs. Dalton Transactions, 2021, 50 (36), pp.12419-12423. 10.1039/D1DT01976G . hal-03396913

HAL Id: hal-03396913

<https://hal.science/hal-03396913>

Submitted on 22 Oct 2021

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Solvothermal and mechanochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$ enabled by the redox reactivity of $(\text{S}_2)^{2-}$ pairs

Received 00th January 20xx,
Accepted 00th January 20xx

Shunsuke Sasaki,^a Gwladys Steciuk,^b Catherine Guillot-Deudon,^a Maria Teresa Caldes,^a Isabelle Braems,^a Etienne Janod,^a Benoît Corraze,^a Stéphane Jobic*^a and Laurent Cario*^a

DOI: 10.1039/x0xx00000x

Intercalation of Cu into layered polychalcogenide $\text{La}_2\text{O}_2\text{S}_2$ was demonstrated to be viable both in solvothermal condition at 200 °C and mechanical ball milling at ambient temperature. This result evidences the soft-chemical nature of metal intercalation into layered polychalcogenides driven by redox reactivity of anion-anion bonds.

Introduction

Soft chemistry (also commonly named *Chimie douce*) is a generic term referring to low-temperature synthetic techniques used to stabilize (meta)stable solid materials.^{1–2} This concerns sol-gel processes as well as (de)intercalation, grafting and pillaring, exchange and condensation, and any route that required low activation energy to access a (new) product.³

Li intercalation is one of the most known soft-chemical processes, which can be performed not only electrochemically but also by the use of *n*-butyllithium in hexane.⁴ The back reaction can be promoted by an oxidising reagent such as iodine.⁵ Longstanding investigations on soft chemical techniques have expanded the scope both of intercalants and host lattices. The use of liquid ammonia for instance made available a wide range of alkaline, alkaline earth elements and even lanthanides as intercalants for graphites,⁶ transition metal dichalcogenides (TMDCs),⁷ superconducting FeSe,⁸ etc. Over the last two decades, extensive efforts have been devoted also to topochemical reactions of anionic species (e.g. oxygen) in perovskite-related compounds.⁹

Recently we proposed to take benefit of the redox-reactivity of chalcogen anions embedded in lamellar compounds (e.g. $\text{La}_2\text{O}_2\text{S}_2$, Fig. 1) to achieve intercalation of transition metal atoms such as Cu, Ni and Fe.^{10–11} This way to proceed differs

significantly from reported mechanisms so far where redox centres are commonly based on cations. Namely, electrons are here transferred from zerovalent metal to chalcogen dimers (or oligomers in general) contained in layered polychalcogenides, leading to the cleavage of the anion-anion bonds and concomitant intercalation of metal cations. This concept was successfully applied to various layered polychalcogenide precursors, i.e. $\text{La}_2\text{O}_2\text{S}_2$, $\text{Ba}_2\text{F}_2\text{S}_2$, LaSe_2 , BaS_2 and BaS_3 , that underwent intercalation of Cu, Fe or Ni to form 3D materials, i.e. $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$, $\text{Ba}_2\text{F}_2\text{Cu}_2\text{S}_2$, LaCuSe_2 , BaNiS_2 and BaFe_2S_3 , at temperatures ($T = 275 - 450$ °C) much lower than the ones used for their synthesis via a conventional ceramic route ($T = 600 - 800$ °C). The topochemical character of the intercalation is highlighted by the clear filiation of the crystal structures between the precursor and the product (Fig. 1).

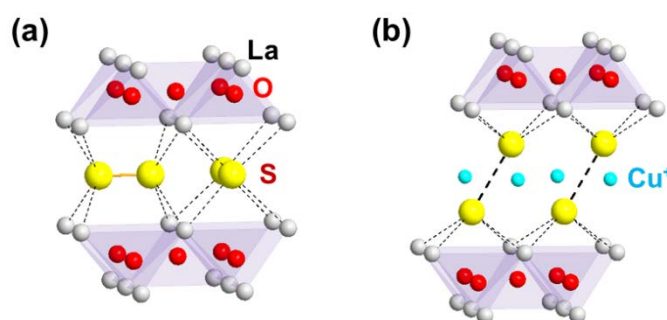


Fig. 1. Structure of (a) $\text{La}_2\text{O}_2\text{S}_2$ and (b) $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ phases highlighting S-S bond cleavage and concurrent sliding of $(\text{La}_2\text{O}_2)^{2+}$ slabs during intercalation of Cu. Due to its significant structural reorganisation, its phase propagation may require larger activation energy than typical intercalation processes.

At this stage, these solid-solid reactions carried out in sealed silica tubes still require a thermal activation, i.e. reactions are promoted clearly at temperatures higher than those used for typical intercalation chemistry in solution or batteries (ca. 300 °C vs. RT). This probably originates here from the necessity to disrupt anion-anion bonds to favor the migration of metal cationic species in the host lattice and the appearance of strong local distortions to accommodate the chemical environment of

^a Université de Nantes, CNRS, Institut des Matériaux Jean Rouxel, IMN, F-44000, Nantes, France.

^b Institute of Physics ASCR, v.v.i., Na Slovance 1999/2, 18221 Praha 8, Czechia.

^c Email: Stephane.Jobic@cnrs-imn.fr, Laurent.Cario@cnrs-imn.fr

† Electronic Supplementary Information (ESI) available:

See DOI: 10.1039/x0xx00000x

the guest. Such distortions may finally trigger the shifting (Fig. 1) of cationic layers constitutive of the host lattice (e.g. $(\text{La}_2\text{O}_2)^{2+}$ slabs in $\text{La}_2\text{O}_2\text{S}_2$) to release constraints. Nevertheless, we wonder whether the intercalation process can be achieved at further lower temperature if a more intimate contact of the reagents is achieved. This may be done by using liquid reaction or by mechanical grinding. In that context, we examined a solution-based chemical route and a soft mechanical one to probe the ability of these processes to end at the topotactic insertion of metal into polychalcogenides with $(\text{S}_n)^{2-}$ redox centres at low temperature. The layered polychalcogenide $\text{La}_2\text{O}_2\text{S}_2$ compound was used as model.

Experimental

Solvothermal intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$

The precursor $\text{La}_2\text{O}_2\text{S}_2$ was prepared as the yellow powder following the method previously reported.¹⁰ CuCl (Aldrich, > 98%), ethylenediamine (Alfa Aesar, 99%) and Cu powder (Alfa Aesar, 100-325 mesh, 99.9%) were purchased and used without further purification. $\text{La}_2\text{O}_2\text{S}_2$ and CuCl were weighed in the 1 : x molar ratios ($x = 2.0, 2.56$ and 4.0) and placed in a 25 mL Teflon-line autoclave. This blend was dispersed in 20 mL of ethylenediamine (en) and the suspension was magnetically stirred for 10 min under inert atmosphere at room temperature. Then the autoclave was assembled and heated at 200 °C for 36 h, followed by a slow cooling to room temperature. The pale-yellow solution was removed from the autoclave by decantation and the grey precipitate was washed repeatedly with ethanol. The washed pale grey powder was dried under vacuum at room temperature.

Mechanochemical ball milling

$\text{La}_2\text{O}_2\text{S}_2$ (prepared as reported in 10) and the Cu powders (Alfa Aesar, 100-325 mesh, 99.9%) were added under argon atmosphere in a 20 mL bowl with 3mm- \varnothing ZrO_2 balls (total number of 41). The balls to powder mass ratio was 4:1. Milling was performed for 20 min at 800 rpm using a Pulverisette 7 Premium Line Fritsch. The mixture underwent a second ball milling treatment in the same conditions but with only three 10mm- \varnothing ZrO_2 balls.

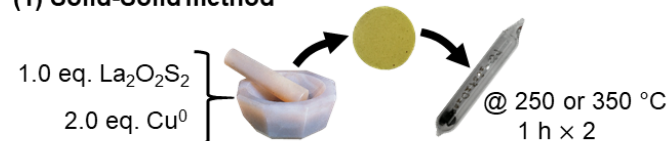
The detailed procedure of X-ray diffraction (XRD) and Transmission electron microscopy (TEM) analyses are described in SI.

Results and discussion

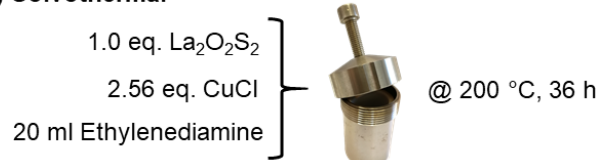
Fig. 2 sketches up the three experimental conditions used to trigger the insertion of Cu into $\text{La}_2\text{O}_2\text{S}_2$ to end at the LaOCuS compound, i.e. the thermal treatment of the ground $\text{La}_2\text{O}_2\text{S}_2/\text{Cu}$ mixture in a sealed silica tube (sample A), the solvothermal treatment of the host lattice $\text{La}_2\text{O}_2\text{S}_2$ with CuCl under autogenous pressure in en (sample B), and the dry ball milling of $\text{La}_2\text{O}_2\text{S}_2/\text{Cu}$ ingredients at room temperature for 2x20 minutes (sample C). Fig. 3 summarises XRD patterns of the

samples A-C, which clearly evidence the conversion of the polysulfide precursor $\text{La}_2\text{O}_2\text{S}_2$ to the Cu-intercalated $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ phase. In the following we discuss the details of each experimental approach.

(1) Solid-Solid method



(2) Solvothermal



(3) Mechanical ball milling

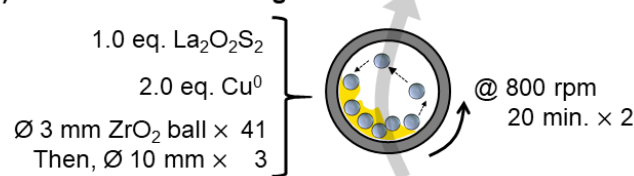


Fig. 2. Overview of different soft-chemical techniques necessary to complete intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$.

We already reported the solid-solid reaction between $\text{La}_2\text{O}_2\text{S}_2$ and metallic Cu powder,¹⁰ which led to the complete conversion of the precursor into the intercalated phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ within two times 1 hour annealing at 250 °C with the intermediate grinding step. The obtained $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ phase featured relatively broad XRD peaks compared to those prepared at high temperature ($T = 700$ °C). In our previous study, we ascribed it, employing Rietveld refinement, to relatively large strain on the crystallites. Herein we performed 3D electron diffraction analysis¹² to provide further insight on the Cu-intercalated phase. Precession electron diffraction tomography (PEDT) data of sample A featured its strong mosaicity (Fig. S1), confirming our previous observation of the cell strain induced by Cu intercalation. Then PEDT data were used for *ab initio* structure solution, which successfully gave a 3D electrostatic potential map (Fig. S2) corresponding to the reported $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ structure.¹³ Further dynamical refinements of the PEDT data converged to $R(\text{obs}) = 0.1261$ and $wR(\text{obs}) = 0.1451$ for 2339 observed reflections with good agreement of the structural parameters (Table S1-S2) with those from our previous Rietveld refinement.¹⁰ Interestingly, our dynamical refinements showed relatively large atomic displacement parameters (ADP) not only for Cu but also S ($U_{\text{iso}} \sim 0.03$ Å³). The large ADP of Cu was reported also in the samples prepared by high-temperature syntheses¹⁴⁻¹⁵ while the one for S atoms may be indicative of structural disorder in antiferro-type $(\text{Cu}_2\text{S}_2)^{2-}$ layers, which stemmed from Cu intercalation.

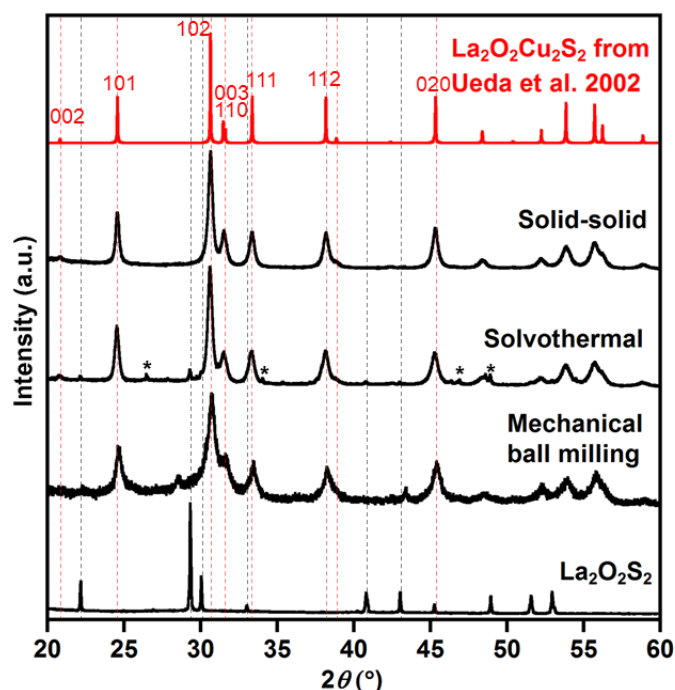


Fig. 3. XRD patterns of $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ phases obtained from solid-solid, solvothetmal and mechanochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$. Each experimental condition is optimized to achieve complete conversion of the precursor $\text{La}_2\text{O}_2\text{S}_2$ into the intercalated phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$. See Fig. 2 and the experimental section for detailed procedure. For comparison, the theoretical XRD pattern of $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ phase was reproduced (red line) with hkl indices of its major reflections using the structure model reported by Ueda et al.¹³ * marks represents Cu_7S_4 phase.²⁵

To access to $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ by solution-based intercalation chemistry protocol, we attempted to couple *in-situ* formation of zerovalent Cu^0 species and intercalation of copper in $\text{La}_2\text{O}_2\text{S}_2$. It is well known that Cu^+ complexes with d^{10} configuration tend to disproportionate into Cu^0 and Cu^{2+} species under the presence of hard base.¹⁶ In particular, ethylenediamine (en) strongly favors the formation of cupric complexes $[\text{Cu}(\text{en})_2]^{2+}$ or $[\text{Cu}(\text{en})_3]^{2+}$ ¹⁷ over their cuprous counterparts.¹⁸ While this disproportionation process is often employed for seeding copper (nano)crystals,¹⁹ Cui and co-workers recently demonstrated also that the *in situ* formed Cu^0 species have the ability to fit into host lattices such as observed for Bi_2Se_3 , MoO_3 , Sb_2Te_3 , In_2Se_3 and GaSe .^{20–21} We can expect a similar result for $\text{La}_2\text{O}_2\text{S}_2$; namely, Cu^0 species formed by disproportionation of Cu^+ salts may react with $(\text{S}_2)^{2-}$ dimers embedded in $\text{La}_2\text{O}_2\text{S}_2$. The generated Cu^0 species may take a form either of molecular Cu^0 complexes or nanoprecipitates deposited onto $\text{La}_2\text{O}_2\text{S}_2$ grains. Practically, the $\text{La}_2\text{O}_2\text{S}_2 + \text{CuCl}$ mixture was heated in an autoclave at 200 °C for 36 h and a grey precipitate was obtained. XRD patterns of these precipitates are shown in Fig. 4. After the thermal treatment, the mixture of $\text{La}_2\text{O}_2\text{S}_2 + 2.0 \text{ CuCl}$ attenuated its XRD peaks from $\text{La}_2\text{O}_2\text{S}_2$ and instead exhibited the relatively broad peaks from $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$. This result clearly evidenced that intercalation of Cu into layered polychalcogenides can take place in solution. Since the disproportionation of Cu^+ species converts only the half of them into Cu^0 species, 2.0 equiv. of CuCl is not sufficient to complete the reaction. Therefore, 4.0 equiv. of CuCl was added in order to complete the conversion

of the precursor into the intercalated phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$. However, this attempt ended up with not only the targeted phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ but also residual metallic copper as a side product, which implied that more than the half of Cu^+ species were converted into Cu^0 species. One possible explanation lies in the possible reduction of generated Cu^{2+} cations in solution by ethylenediamine itself. In fact, some aliphatic amines such as Oleylamine are often employed to reduce Cu^+ nor Cu^{2+} salts during the syntheses of Cu nanoparticles.^{22–23} Given these results, the most straightforward way to control Cu^0 stoichiometry is to regulate feed of the CuCl salt. Our Rietveld refinement revealed that *ca.* 78 mol% of $\text{La}_2\text{O}_2\text{S}_2$ was converted into $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ by 2.0 equiv. of CuCl in ethylenediamine. It corresponds to the formation of 1.56 equiv. of Cu^0 species from 2.0 equiv. of CuCl salt. Accordingly, 2.56 equiv. of CuCl was estimated to be the requisite amount to consume all the precursor $\text{La}_2\text{O}_2\text{S}_2$. As expected, the thermal treatment of $\text{La}_2\text{O}_2\text{S}_2 + 2.56 \text{ CuCl}$ in *en* ($T = 200^\circ\text{C}$) almost fully converted the polychalcogenide precursor into the intercalated phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ without leaving any residual Cu^0 metal (Fig. 3). The obtained XRD pattern is almost identical with the one obtained by solid-solid reaction in the sealed silica tubes and accordingly it features relatively broad peak profiles compared to those from high-temperature syntheses.^{10,13}

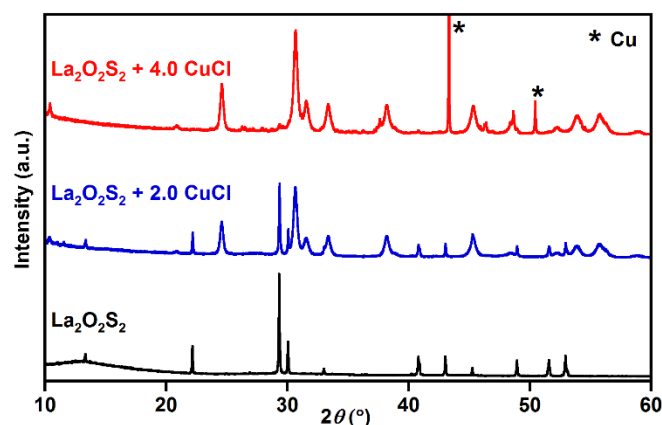


Fig. 4. XRD patterns obtained from the solvothetmal reaction between $\text{La}_2\text{O}_2\text{S}_2$ and CuCl in ethylenediamine at 200 °C.

As a whole, we successfully demonstrated that the topochemical intercalation of Cu into $(\text{S}_2)^{2-}$ containing materials can proceed even by the solution-based method. Since Cu^0 species in solution can access every grain of $\text{La}_2\text{O}_2\text{S}_2$, the reaction is very efficient and does no longer require multiple thermal treatment unlike the solid-solid method. As shown in XRD pattern of the $\text{La}_2\text{O}_2\text{S}_2 + 2.0 \text{ CuCl}$ mixture (Fig. 4), the thermal treatment in ethylenediamine did not dissolve $\text{La}_2\text{O}_2\text{S}_2$, rejecting the dispersion/flocculation process²⁴ from the plausible mechanisms of $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ formation. This solvothetmal reaction between $\text{La}_2\text{O}_2\text{S}_2$ and Cu^0 species selectively yielded the targeted quaternary phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ regardless of stoichiometry apart from trace amount of impurity phase Cu_7S_4 which may stem from partial desulfurization of the $\text{La}_2\text{O}_2\text{S}_2$ polysulfide under the presence of excess Cu^0 species.²⁶ This observation is in sharp contrast to our

previous solvothermal synthesis of $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$ starting from $\text{LaCl}_3 \cdot 0.3\text{H}_2\text{O}$, CuO , Cu_2O and S that required a very strict control of stoichiometry and hydration of precursors to avoid undesirable by-products.²⁷ This selectivity reflects the topochemical nature of our current example of solvothermal intercalation.

Mechanical ball milling often activates solid-state reactions such as polymorphic transformation, alloying, decomposition involving gaseous products and topotactic reactions through the creation of energetically active surfaces with rupture of bonds.²⁸ In this context, topochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$, which possibly involves minimal movements of its structural units,^{10–11} should be an attractive subject for mechanochemistry.

Therefore, we examined the mechanochemical reaction of $\text{La}_2\text{O}_2\text{S}_2$ and Cu employing planetary ball milling. The collected XRD pattern of the mixture is depicted in Fig. 3. After 2×20 minutes of grinding, XRD peaks of $\text{La}_2\text{O}_2\text{S}_2$ have almost disappeared and are replaced by broad peaks of $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$. This result clearly demonstrates that also the mechanical ball milling can activate the topochemical intercalation of Cu into $(\text{S}_n)^{2-}$ containing materials. However, we cannot completely rule out the possibility of thermal activation as driving force of the reaction. Typically, the temperature in a vial goes up to 50–120 °C during ball milling²⁹ but it is much lower than the reaction temperature of our topochemical insertion, i.e. 250–350 °C.¹⁰ On the other hand, microscopic temperature that are inferred from microstructural and/or crystal structure change during milling may rise much more than these measured temperatures in a moment of e.g. collision.³⁰

Conclusions

This study demonstrated that the topochemical intercalation of Cu into $\text{La}_2\text{O}_2\text{S}_2$ can proceed also under the solvothermal and mechanochemical conditions. In the solvothermal approach, $\text{La}_2\text{O}_2\text{S}_2$ reacts with Cu^0 species generated *in-situ* through disproportionation of Cu^+ species, yielding the corresponding quaternary phase $\text{La}_2\text{O}_2\text{Cu}_2\text{S}_2$. Such insertion of copper was achieved also by mechanical ball milling of $\text{La}_2\text{O}_2\text{S}_2$ with the metallic copper. These two results reflect the topochemical nature of the reaction between transition metals and $(\text{S}_n)^{2-}$ containing materials. In addition, both attempts are conducted at significantly lower temperature ($T = 200$ °C and r.t. for solvothermal and mechanosynthesis, respectively) than the solid-solid process ($T = 250$ – 350 °C), which makes the topochemical intercalation more promising as a tool to explore metastable phases.

Conflicts of interest

There are no conflicts to declare.

References

- J. Rouxel and M. Tournoux, *Solid State Ionics*, 1996, **84**, 141–149.
- F. J. DiSalvo, *Solid. State Commun.* 1997, **102**, 79–85.
- J. Gopalakrishnan, *Chem. Mater.* 1995, **7**, 1265–1275.
- D. W. Murphy, P. A. Christian, *Science* 1979, **205**, 651–656.
- D. W. Murphy, C. Cros, F. J. DiSalvo, and J. V. Waszczak, *Inorg. Chem.* 1977, **16**, 3027–3031.
- R. Setton, 9. Ternary systems. In *Graphite Intercalation Compounds I –Structure and Dynamics*, H. Zabel and S. A. Solin eds., Springer, Springer Series in Materials Science, M. Cardona (ed.), Berlin, 1992, **14**, pp309–345.
- R. B. Somoano, V. Hadek, and A. Rembaum, *J. Chem. Phys.* 1973, **58**, 697–701.
- T. P. Ying, X. L. Chen, G. Wang, S. F. Jin, T. T. Zhou, X. F. Lai, H. Zhang and W. Y. Wang, *Sci. Rep.* 2012, **2**, 426.
- K. G. S. Ranmohotti, E. Josepha, J. Choi, J. Zhang and J. B. Wiley, *Adv. Mater.* 2011, **23**, 442–460.
- S. Sasaki, D. Driss, E. Grange, J.-Y. Mevellec, M. T. Caldes, C.-G. Deudon, S. Cadars, B. Corraze, E. Janod, S. Jobic and L. Cario, *Angew. Chem. Int. Ed.* 2018, **57**, 13618.
- S. Sasaki, M. Lesault, E. Grange, E. Janod, B. Corraze, S. Cadars, M. T. Caldes, C.-G. Deudon, S. Jobic, and L. Cario, *Chem. Commun.* 2019, **55**, 6189.
- M. Gemmi, M. Mugnaioli, T. E. Gorelik, U. Kolb, L. Palatinus, P. Boullay, S. Hovmöller, and J. P. Abrahams, *ACS Cent. Sci.* 2019, **5**, 1315–1329.
- K. Ueda and H. Hosono, *Thin Solid Films* 2002, **411**, 115–118.
- M. Palazzi, *Acad. Sci., Paris, C. R.* 1981, **292**, 789–791.
- W. J. Zhu, Y. Z. Huang, C. Dong, Z. X. Zhao, *Mater. Res. Bull.* 1994, **29**, 143.
- M. A. Rizvi, *Russ. J. Gen. Chem.* 2015, **85**, 959–973.
- Y. Inada, K. Ozutsumi, S. Funahashi, S. Soyama, T. Kawashima and M. Tanaka, *Inorg. Chem.* 1993, **32**, 3010–3014.
- K. Srinivasan and R. S. Subrahmanya, *J. Electroanal. Chem.* 1971, **31**, 257–263.
- H. Guo, X. Liu, Q. Xie, L. Wang, D.-L. Peng, P. S. Brancob and M. B. Gawande, *RSC Adv.* 2013, **3**, 19812–19815.
- K. J. Koski, C. D. Wessells, B. W. Reed, J. J. Cha, D. Kong and Y. Cui, *J. Am. Chem. Soc.* 2012, **134**, 13773–13779.
- J. P. Motter, K. J. Koski, Y. Cui, *Chem. Mater.* 2014, **26**, 2313–2317.
- M. A. Ben Aissa, B. Tremblay, A. A.-Ledier, E. Maisonhaute, N. Raouafi and A. Courty, *Nanoscale* 2015, **7**, 3189–3195.
- S. Mourdikoudis and L. M. Liz-Marzán, *Chem. Mater.* 2013, **9**, 1465–1476.
- L. Beneš, K. Melànovà, V. Zima, J. Kalousová, J. Votinský, *J. Inclusion Phenom. Mol. Recognit. Chem.* 1998, **31**, 275–286.
- K. Koto and N. Morimoto, *Acta Cryst.* 1970, **B26**, 915–924.
- S. Sasaki, M. T. Caldes, C. G.-Deudon, I. Braems, G. Steciuk, L. Palatinus, E. Gautron, G. Frapper, E. Janod, B. Corraze, S. Jobic and L. Cario, *Nat. Commun.* 2021, **12**, 3605.
- C. D.-Brochard, B. Chavillon, L. Cario and S. Jobic, *Inorg. Chem.* 2010, **49**, 3074–3076.
- I. J. Lin and S. Nadiv, *Mater. Sci. Eng.* 1979, **39**, 193–209.
- C. Suryanarayana, *Prog. Mater. Sci.* 2001, **46**, 1–184.
- A. Tonejc, M. Stubicar, A. M. Tonejc, K. Kosanovic, B. Subotic, I. Smit, *J. Mater. Sci. Lett.* 1994, **13**, 519–20.