Polymer Intercalation into Layered Materials

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Abstract

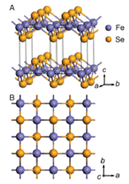
The overall goal of this research was to discover new superconducting materials from intercalation of polymers into layered compounds with a Van der Waals gap. Specifically, conducting polymers, polyaniline (Pan), polythiophene (PT), and polypyrrole (Ppy) were used in order to manipulate their conjugated bonds to transfer electric charges efficiently.

The layered compounds have attracted more attention because of their interesting physical properties induced by dimensionality; such as superconductivity, quantum criticality, etc. The existence of a Van der Waals gap in such kind of compounds makes them good candidates for an intercalation study, during which the crystal structure is slightly tuned and the properties are expected to change correspondingly.

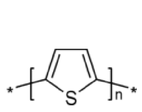
In this experiment, monomers of conducting polymers were intercalated into layered materials FeSe and FeTe, then polymerized through *in situ* oxidation using ammonium persulfate. Our results indicate the polymer intercalation changes crystal structure and physical properties.

Introduction

Recent developments in the field of inorganic superconducting layered materials coupled with a shift in attention to organic compounds that display electrochemical and electrochromic properties has led to an increased awareness of possibilities for hybrid organic-inorganic materials. (1, 2) As a result of this rising interest and the unexplored nature the field, we are seeing a variety of novel techniques being developed to synthesize these hybrid compounds and ascertain their physical and electrical properties. While these nanocomposites have a wide range of applications, for example, in non-linear optics, as nanowires, sensors, and light-weight reinforced structures, the goal of this project is to investigate the potential of the composites as plastic superconductors. (2) Because the resultant hybrid materials derive many characteristics from their parent compounds, such as critical temperature and quantum criticality, leads to a selection of components that are inherently superconducting and electroactive at some level.



Layered compound



Polythiophene

Thus, the process is a fundamentally enhancing one. There remains, however, a possibility that properties foreign to the parents may be discovered. The hope is that any new properties would result in bulk superconductivity, especially at increased temperatures relative to the host inorganic compound. (1,2) Four methods in particular have been employed to intercalate polymers into target samples: initially inserting monomers in between layers followed by respective polymerization, by *in situ* intercalative oxidation, direct polymer injection, and by encapsulate precipitation. (3) This presentation reports the preparation of polyaniline (Pan) and polythiophene (PT), the methodology of intercalation, namely *in situ* oxidation, and the properties of the resultant materials with FeSe as the inorganic host. Property characterization was conducted by X-ray diffraction and SQUID analysis.

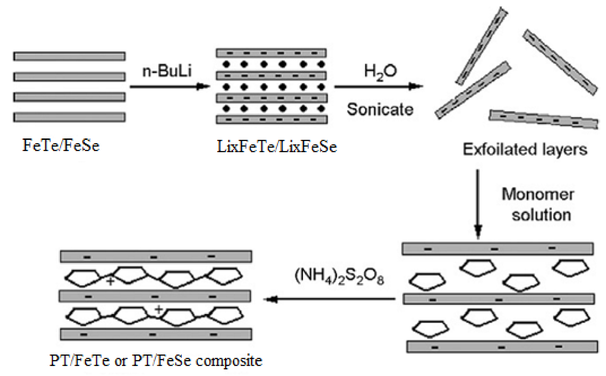
Methods – Intercalation via Potassium

This method of first intercalating potassium into the layered compound is carried out through a solid state reaction.

1) Add potassium, iron, tellurium/selenium in a 0.8 : 2 : 2 molar ratio in a Pyrex tube
2) Heat the mixture to 950°C over a 24 hour period
3) Cool the compound slowly
4) For the rest of the procedure, reference steps 5 – 15 in the lithium intercalation method

Methods- Intercalation via Lithium

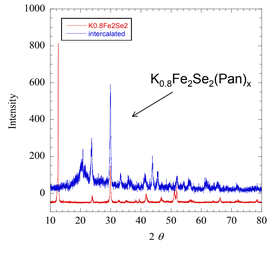
1) Mix 3.125mmol of layered compound and 4mL of 2M n-BuLi in cyclohexane in a Schlenk line.
2) Heat at 80°C for 4 hours
3) Filter the product and wash with anhydrous hexane
4) Dry in vacuum at room temperature
5) Add 1g Li_x(layer compound) in 20mL H_2O
6) Sonicate at ambient temperature for 2 hours
7) Neutralize the solution with dilute acid (1M nitric acid)
8) Add 1g monomer dissolved in 20mL N-methylformaminde/water mixed solvent (1:1, v/v)
9) Drop monomer solution into monolayer suspension under mechanical stirring for 2 hours
10) Add 3g $(NH_4)_2S_2O_8$ in 20mL H_2O to the mixture.
11) Modify the pH of the mixture to 4 - 5 using nitric acid
12) Keep under controlled temperature of 50°C for 12 hours
13) Centrifuge the mixture at 4000rpm for 30 minutes
14) Wash the product several times with NMF and water
15) Dry product under suction and then freeze-dry

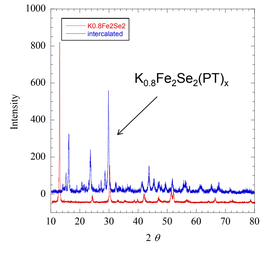


Scheme 1. Preparation procedure for PT/Layered compound intercalation material

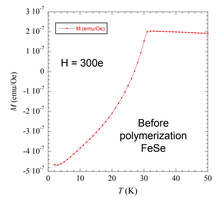
Results and Discussion

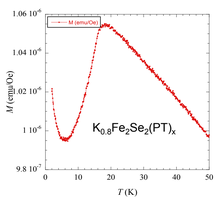
- The X-ray diffraction measurements point to a successful chemical intercalation
  - Shifted peaks seen in both samples
- The structure of the polyaniline intercalate is simpler than that of the polythiophene
  - Less peaks

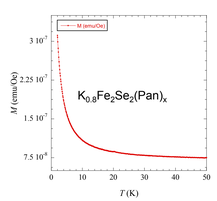




- The initial layered compound (FeSe) shows a superconducting transition at T_c=30K
- The polythiophene sample displays complex magnetic properties
  - Non-monotonic
  - Might be due to impurities in the sample
- The polyaniline compound exhibits ferromagnetism







Conclusion and Future Work

- Based on the pre and post XRD scans of the intercalated compounds, it can be deduced that a chemical intercalation did take place
  - Proved by the shift in the intensity peaks on the scans
- The magnetometer measurements point to a change in magnetic properties of the host materials upon intercalation
- Future polymer intercalations should take place in de-gassed H_2O because the oxygen in the atmosphere inhibits the polymerization reaction
- More efficient methods to separate the solvents from the product must be developed
- The degree of lithiation must still be determined as well as the stoichiometric amount of polymer intercalated into the layered compound

References

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