Synthesis and Characterisation of Lithium Silicides

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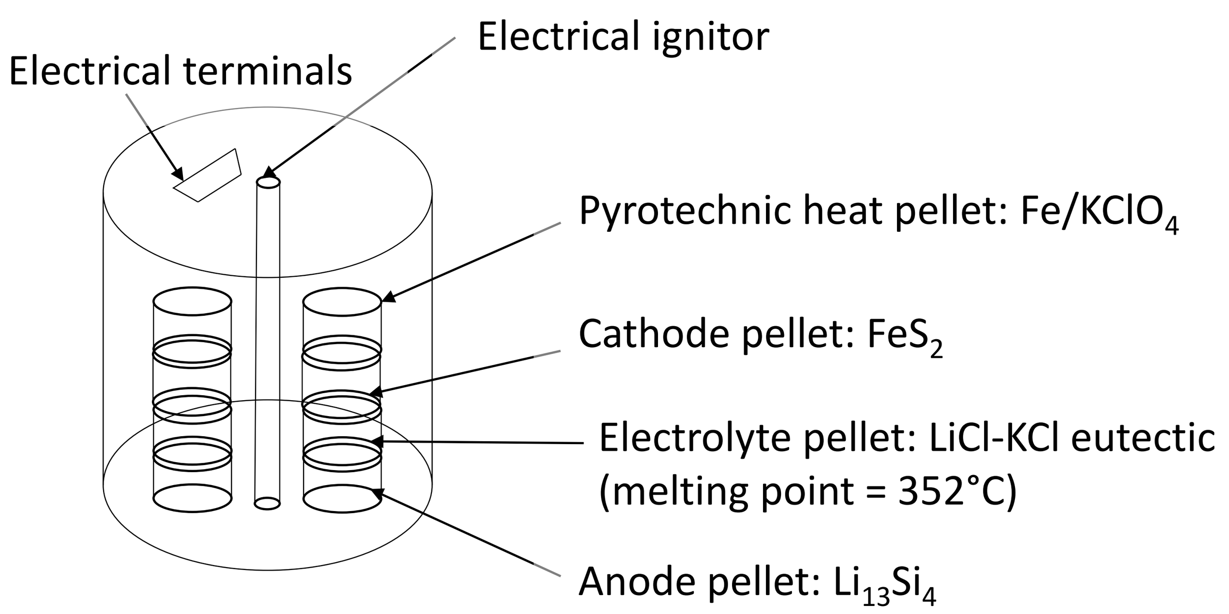
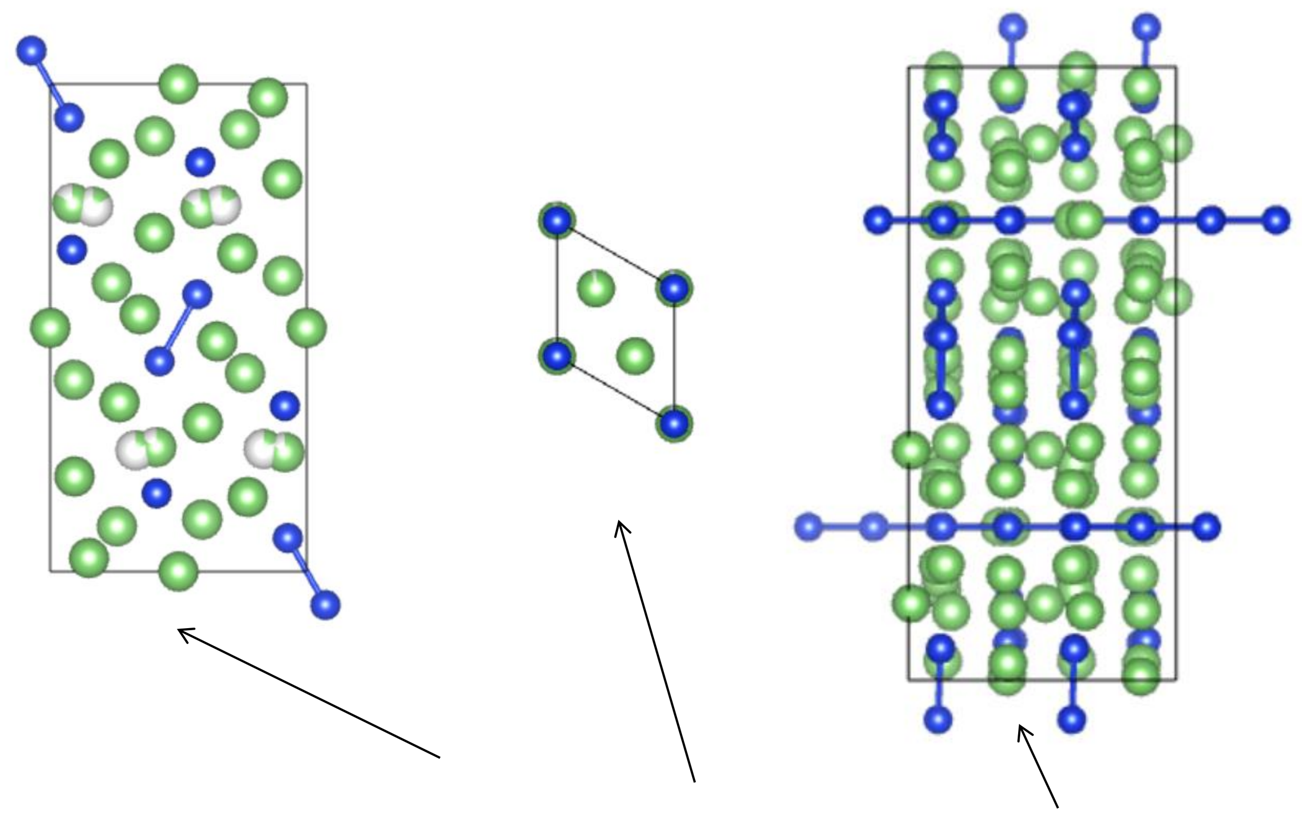
1. Thermal Batteries



Thermal batteries are used in aircraft emergency power supplies, space exploration, borehole drilling and military applications. This is because they are robust, reliable and have a long shelf life.

Thermal batteries are primary (non-rechargeable) batteries. To activate the battery, a pyrotechnic heat source melts the solid electrolyte to a molten salt at high temperature (typically around 500°C).

2. Anode Materials for Thermal Batteries

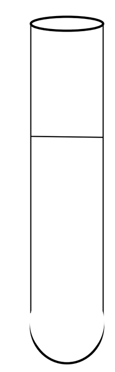


$Li_{21}Si_5$ ($Li_{4.4}Si$) → $Li_{13}Si_4$($Li_{3.25}Si$) → Li_7Si_3($Li_{2.33}Si$) → $Li_{12}Si_7$($Li_{1.71}Si$)

Thermal battery discharge

The four thermodynamically stable phases of the lithium-silicon system are shown above. $Li_{13}Si_4$ is the preferred anode material for thermal batteries. $Li_{13}Si_4$ and other lithium-silicon phases are of interest because the high temperature structures and phase transitions have not been studied systemically.

3. Synthesis



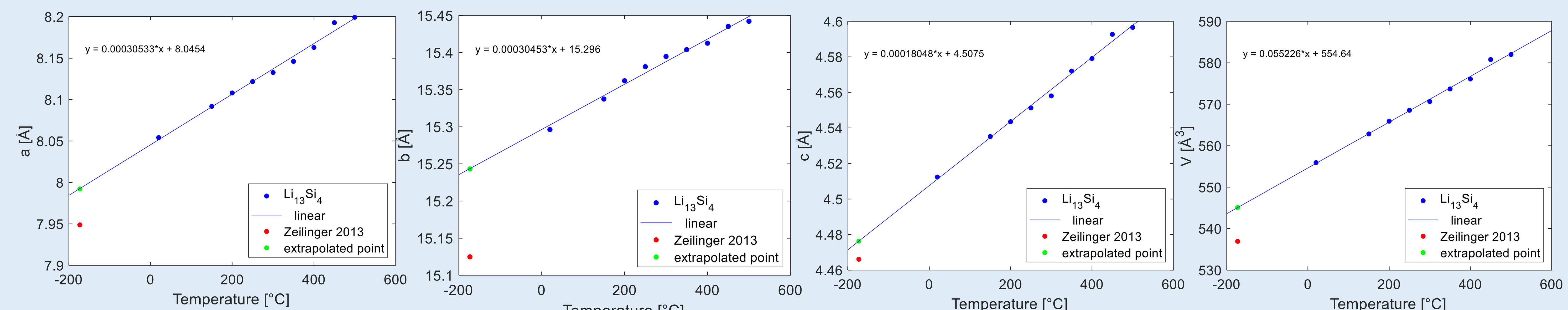
1. 1g of lithium metal and silicon powder were mixed in the stoichiometric ratio.
2. The mixture was wrapped in tantalum foil and this was placed in a quartz tube. The tube was evacuated and sealed with a high temperature flame.
3. The sealed tube was placed in a tube furnace. Lithium was melted at 180.5°C for 2 hours. The mixture was heated at 500°C for 12 hours [1]. The reaction was cooled and quenched at below 180°C.

4. Neutron Diffraction

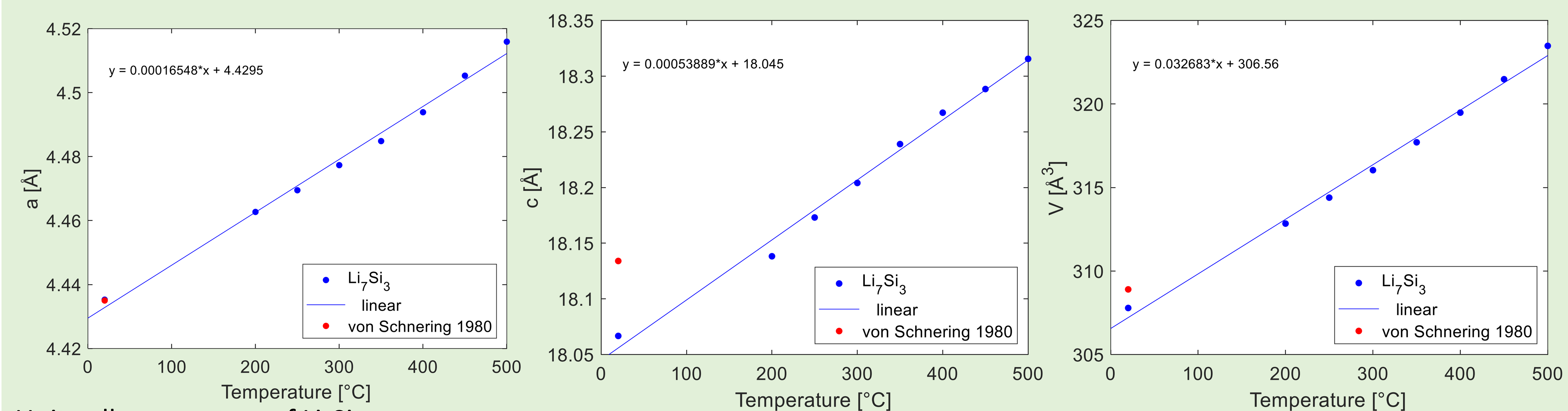
The unit cell parameters for $Li_{13}Si_4$ in the literature by Zeilinger et al. are smaller than that observed in this work [3].

On the other hand, the unit cell parameters for Li_7Si_3 by von Schnering et al. are larger than that observed in this work, although the cell parameter a at room temperature matches very well with that measured by von Schnering et al [2].

The figures below show the trend of the cell parameters is linear. The neutron data indicates that there are no phase transitions between room temperature and 500°C. Both phases are not amorphous at 500°C and the unit cells for both phases expand as the temperature increases.

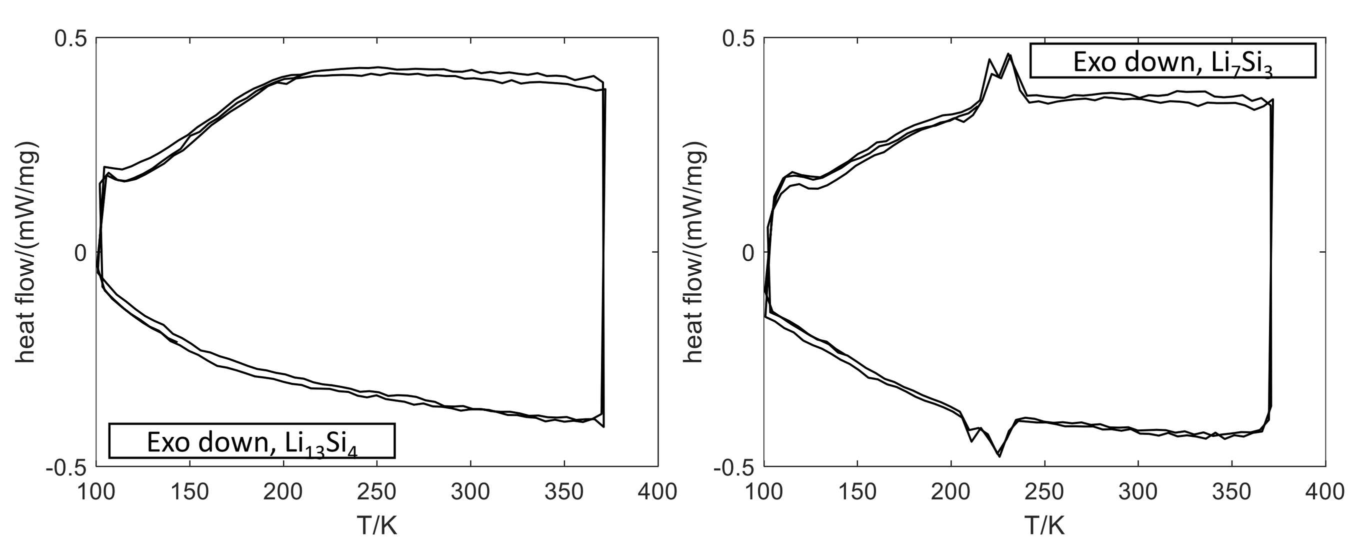


Unit cell parameters of $Li_{13}Si_4$.



Unit cell parameters of Li_7Si_3.

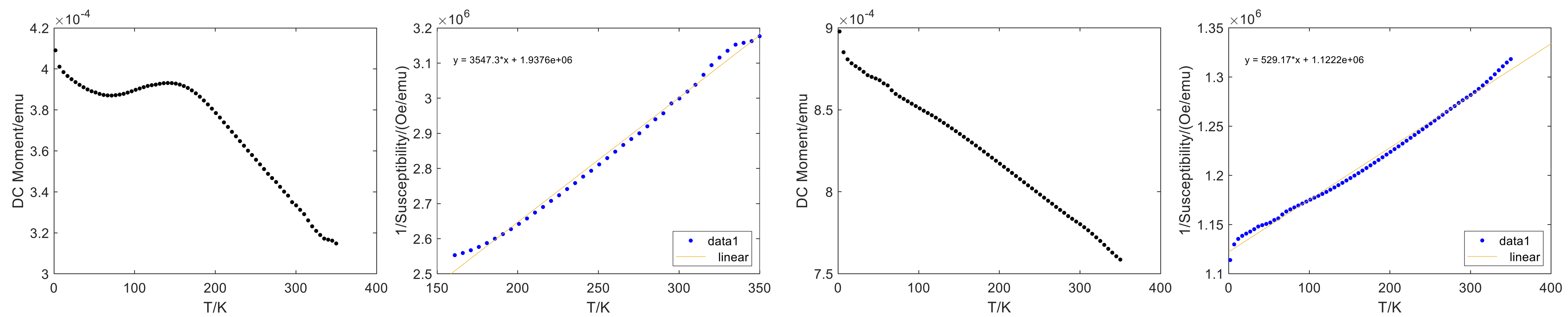
5. Differential Scanning Calirometry



The DSC thermogram showed no peaks for $Li_{13}Si_4$.

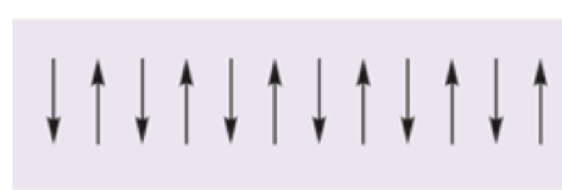
The thermogram showed two exothermic peaks and two endothermic peaks between 200 and 250K for Li_7Si_3.

6. Magnetic Measurements



At around 150K there is a transition in the $Li_{13}Si_4$ phase.

The magnetic ordering temperature is the intercept with the x-axis of the 1/susceptibility versus temperature graph. The magnetic ordering temperature is negative for both phases, so both are antiferromagnetic (unpaired electrons line up opposite one another as shown in the diagram).



7. References

1. B. Key, R. Bhattacharyya, M. Morcrette, V. Seznéc, J. Tarascon and C. Grey, Journal of the American Chemical Society, 2009, 131, 9239-9249.

2. H. Von Schnering, R. Nesper, K. Tebbe and J. Curda, Chemischer Informationsdienst, 1980, 11.

3. M. Zeilinger and T. Fässler, Acta Crystallographica Section E Structure Reports Online, 2013, 69, i81-i82.

8. Acknowledgements

The authors acknowledge AWE for funding and supporting the project.