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Synthesis and structure of ALaTiO4 and A2La2Ti3O10 (A = Na¬+, K+) Ruddlesden-Popper type photocatalysts

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Global warming is a current hot topic due to its potential for irreversible environmental damage. Ambitions were made within the Paris agreement to limit the temperature rise to be below 1.5 ºC pre-industrial level. Alternative fuel sources are needed to replace fossil fuel, reducing the emission of greenhouse gases including CO2. Hydrogen gas is one popular choice to replace fossil fuels, due to its high energy density per unit weight, with existing technologies utilising hydrogen as energy generator. Hydrogen can be generated renewably by sunlight driven, photocatalytic water-splitting. Metal oxides, including those with a Ruddlesden-Popper type structures are being studied as potential photocatalysts. The structure's multiple cationic sites, which allows for different combinations of metal cations that can be used to adjust the bandgap. The layered structuring also allows for the intercalation of different cations within the structure that allows for modifications post synthesis. KLaTiO4 is a n=1 Ruddlesden-Popper type layered perovskite. KLaTiO4 can be used as a Hydrogen Evolution Catalyst (HEC), producing 9.540 mol of H2 gas per hour from 20 mg of catalyst, when using methanol as sacrificial electron donor and platinum co-catalyst.
KLaTiO4 was prepared using traditional solid-state chemistry methods to provide a sample for both catalytic testing and structural studies using neutron diffraction. Synthesis of KLaTiO4 above 900 °C resulted in the presence of K2La2Ti3O10 impurity in the product. K2La2Ti3O10 is structurally similar to KLaTiO4, both being layered perovskite of the Ruddlesden-Popper type structure, with layers of TiO6. The main difference between the two is KLaTiO4 has 1-layer of perovskite-like TiO6 blocks, while K2La2Ti3O10 has 3-layer perovskite slabs. The sodium analogues, NaLaTiO4 and Na2La2Ti3O10 can also be made and these are isostructural to their potassium counterparts.
In this presentation, two factors important for the synthesis of ALaTiO4 and A2La2Ti3O10 (A = Na¬+, K+) will be discussed. The first factor to consider is the volatility of alkaline metal ions at elevated temperatures. Due to this volatility, excess Na or K needs to be included in the initial reagent mixture. Ex-situ XRD measurements showed that if the excess of Na2CO3 was limited to 10%, neither NaLaTiO4 nor Na2La2Ti3O10 could be made. Successful synthesis of NaLaTiO4 or Na2La2Ti3O10 required 50 % (minimum tested) alkaline metal reagent excess. The second factor to consider is related to sintering temperature. Multiple samples of NaLaTiO4 or Na2La2Ti3O10 were made using traditional solid-state synthesis methods at temperature between 750 °C to 950 °C. Incomplete reaction was observed if the temperature was kept below 750 °C during the synthesis, XRD revealing unreacted La2O3, as well as other unidentified impurities. It was also discovered that when reagents with the stoichiometry to make NaLaTiO4 (with Na2CO3 excess) were sintered above 900 °C Na2La2Ti3O10 impurities were present, which is a lower temperature than most literature reports. Finally, Na2La2Ti3O10 was made at 800 °C, which is lower than other literature reports, and the temperature which NaLaTiO4 was found to be made at good purity.

Level of Expertise

Student

Speakers Gender

Male

Do you wish to take part in the poster slam

Yes

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