Synthesis and structure of $KLaTiO_4$ and $NaLaTiO_4$ Ruddlesden-Popper type photocatalysts for water-splitting

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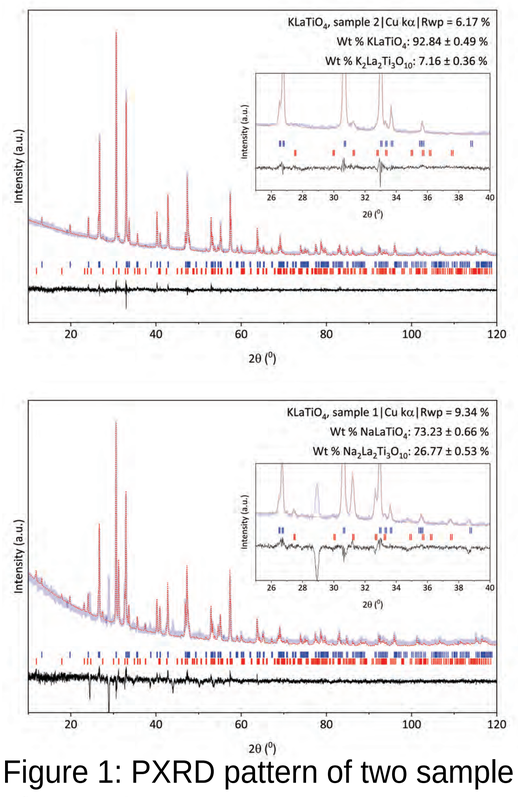

Figure 1: PXRD pattern of two sample of $KLaTiO_4$.

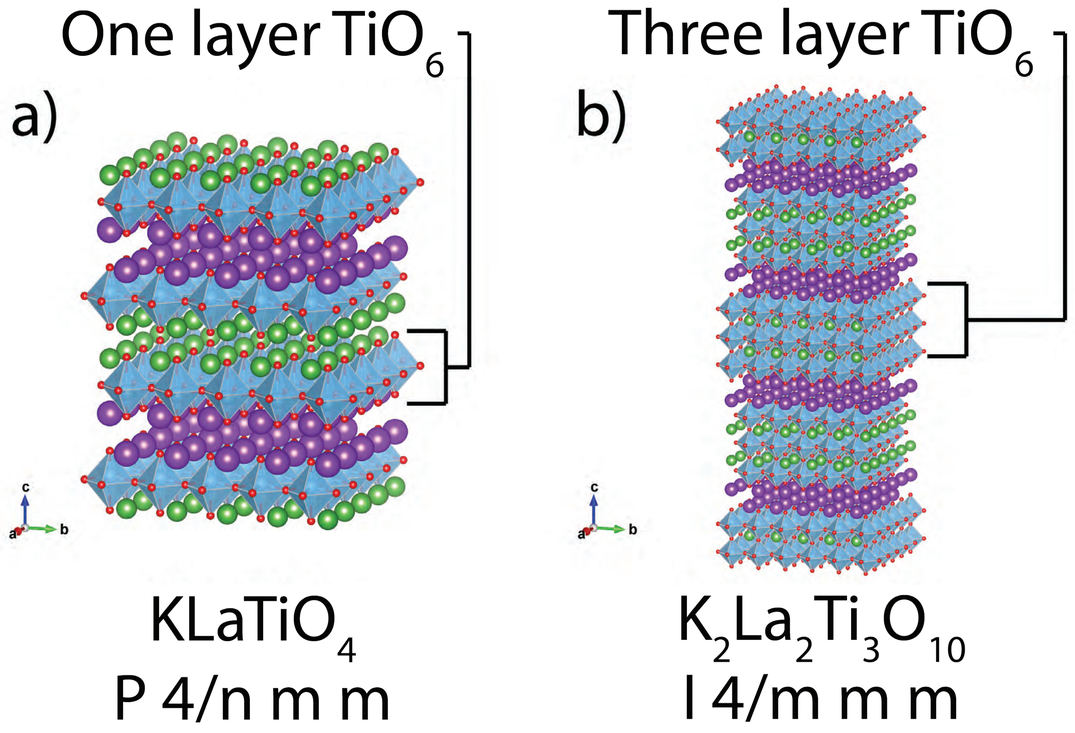

Figure 2: Model structures of a) $KLaTiO_4$, which has a n=1 RP type structure and b) $K_2La_2Ti_3O_{10}$, which has a n=3 RP type structure, with TiO_6 perovskites layers separated by rock salt layer of potassium (purple) and lanthanum (green).

Introduction

Global warming is a current hot topic due to its potential for irreversible environmental damage. Renewable energy sources such as hydrogen are needed. $KLaTiO_4$ can be used as photocatalyst for hydrogen evolution, producing 9.540 µmol of H2 gas per hour from 20 mg of catalyst.

$KLaTiO_4$ was made by heating reagent mixture at 950 °C for 30 minutes, with 55% KNO_3 excess[1, 2]. $K_2La_2Ti_3O_{10}$ impurity were found, as seen in figure 1. $K_2La_2Ti_3O_{10}$ is a known photocatalyst for hydrogen gas evolution[3], therefore, accurate deduction of phase composition is important.

$K_2La_2Ti_3O_{10}$ and $KLaTiO_4$, are both Ruddlesden-Popper (RP) type layered perovskites as seen in figure 2, with $KLaTiO_4$ containing 1-layer of TiO_6 perovskites, while $K_2La_2Ti_3O_{10}$ has 3-layers thick perovskite slabs.

Synthesis of $NaLaTiO_4$

$NaLaTiO_4$ and $Na_2La_2Ti_3O_{10}$ are isostructural to their potassium counterparts, with first synthesis reported by G. Blasse in 19684 using a sintering temperature of 1000 °C.

Four samples of $NaLaTiO_4$ were made, with the phase composition of the samples shown in figure 3, demonstrating sintering temperature of 800 ºC result in yield of 98 % $NaLaTiO_4$ by weight.

More samples were made to test the effect of repeated sintering, amount of Na_2CO_3 excess and reagent packing density have on the yield of $NaLaTiO_4$. The results are summarised in figure 4.

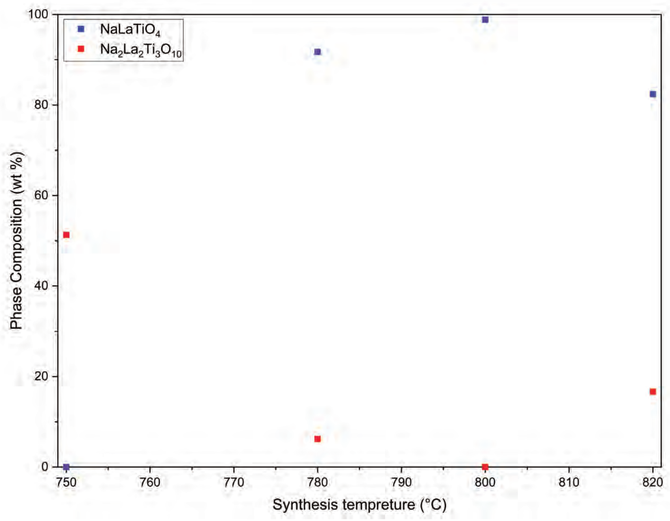

Figure 3: Phase composition of $NaLaTiO_4$ (blue) and $Na_2La_2Ti_3O_{10}$ (red) vs sintering temperature.

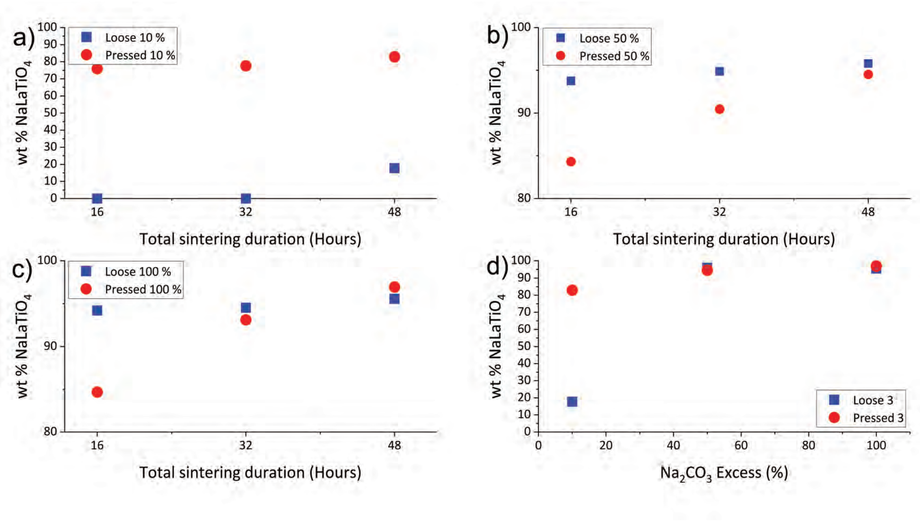

Figure 4: Weight percentage of $NaLaTiO_4$. Sample was made with a) 10 % Na_2CO_3 excess, b) 50 % Na_2CO_3 excess and c) 100 % Na_2CO_3 excess. d) Weight percentage of $NaLaTiO_4$ vs Na_2CO_3 excess added after 48 hours sintering.

Synthesis of $KLaTiO_4$

$KLaTiO_4$ samples were made with different amount of excess KNO_3, which were sintered between 750 - 1000 ºC. The weight percentage of $KLaTiO_4$ are plotted in figure 5.

Samples were found to contain ~ 95 % $KLaTiO_4$ when the reagents contained 50 % or above KNO3 excess was sintered at 800 ºC or 850 ºC. This suggest optimal synthesis temperature of $KLaTiO_4$ to be between 800 - 850 ºC.

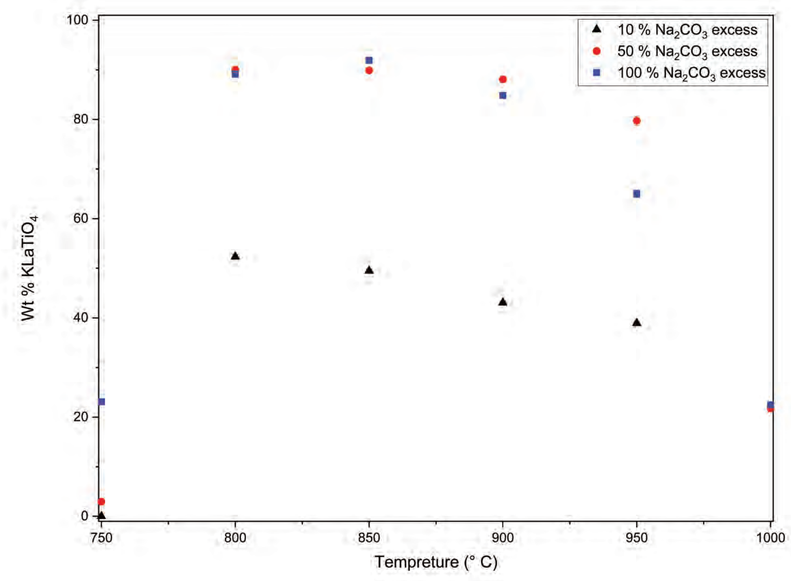

Figure 5: Phase composition of $KLaTiO_4$ vs sintering temperature.

Phase Quantification of $KLaTiO_4$ and $NaLaTiO_4$

In order to determine sample purity of both $KLaTiO_4$ and $NaLaTiO_4$, Neutron Powder Diffraction (NPD) patterns were obtained, shown in figure 6.

In both PXRD and NPD patterns of $KLaTiO_4$, $K_2La_2Ti_3O_{10}$ impurities was seen. Phase composition of the sample listed in table 1. $KLaTiO_4$ was found to be hydrated.

Impurities of $Na_2La_2Ti_3O_{10}$ and La_2O_3can be found in both PXRD and NPD patterns of $NaLaTiO_4$. Na2CO3 was only apparent in NPD pattern. The phase composition of NaLaTiO4 is shown in table 2.

Table 1: Phase composition of $KLaTiO_4$ as determined by combined Rietveld refinement of PXRD and NPD pattern.

Phase	Weight fraction (%)
$KLaTiO_4.xH_2O$	91.72
$K_2La_2Ti_3O_{10}$	8.28

Table 2: Phase composition of $NaLaTiO_4$ as determined by combined Rietveld refinement of PXRD and NPD pattern.

Phase	Weight fraction (%)
$NaLaTiO_4$	91.66
$Na_2La_2Ti_3O_{10}$	3.89
La_2O_3	0.54
Na_2CO_3	3.91

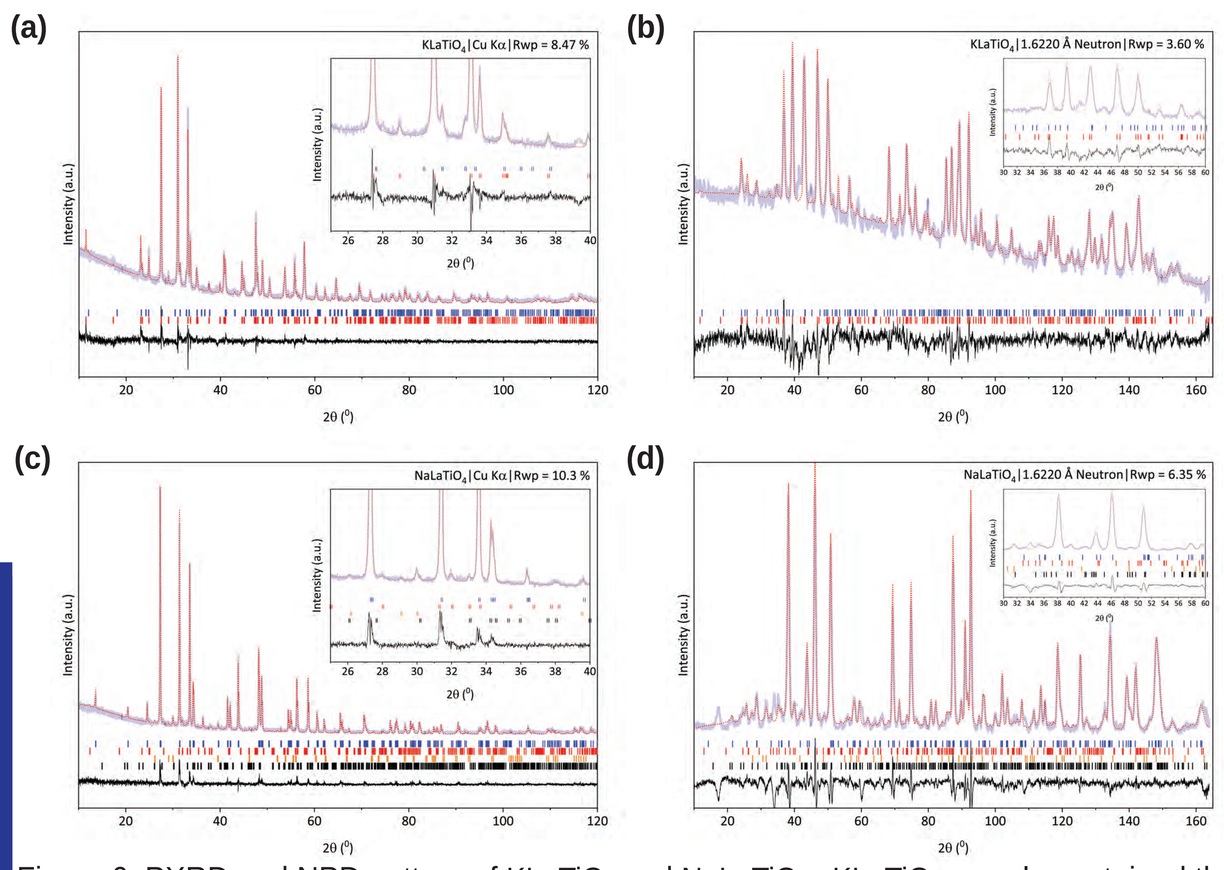

Figure 6: PXRD and NPD pattern of $KLaTiO_4$ and $NaLaTiO_4$. $KLaTiO_4$ sample contained the hydrated $KLaTiO_4$ .xH_2O (blue), as well as $K_2La_2Ti_3O_{10}$ (red). $NaLaTiO_4$ sample contained $NaLaTiO_4$ (blue), $Na_2La_2Ti_3O_{10}$ (red), La_2O_3 (orange) and Na_2CO_3 (black). NPD were collected using Echidna instrument in ANSTO.

Conclusion

Yield of 92 % was achieved for $KLaTiO_4$ and $NaLaTiO_4$. Factors for synthesis of both samples to be synthesis temperature and alkaline excess in the reagent.

References

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