



Layered Dion-Jacobson type niobium oxides for photocatalytic hydrogen production prepared via molten salt synthesis



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ABSTRACT

A class of Dion-Jacobson type layered perovskite niobium oxides ($AB_2Nb_3O_{10}$ with $A = K, Rb, Cs$ and $B = Ca, Sr, Ba$) was prepared via molten salt method for the first time. By dissolving oxide and carbonate precursors in A-cation chloride melts, this type of synthesis needs only two hours of preparation time resulting in highly crystalline layered niobates at a much shorter synthesis time compared to conventional syntheses, like the solid state reaction. Beside detailed materials characterization, we investigated the influence of A-cation and B-cation variation on the band gap and photocatalytic activity for hydrogen production. It was found that the band gap decreases with the increase in size of the B-cation. A strong dependence on interlayer spacing (influenced by the size of the A-cation) and lattice relaxation can be derived from the steady-state hydrogen evolution rates.

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1. Introduction

The rising global population, together with the increasing demand for clean energy and shortening fossil fuel resources, requires the development of technologies allowing the conversion of solar light into energy and solar fuels. Water splitting using photocatalytic materials active both in UV and visible light is often discussed as a promising way of hydrogen production as a clean fuel [1,2]. To achieve this, stable photocatalysts with high activity, suitable band positions and band gap energy are needed [3]. Specifically, the conduction band minimum of such catalysts has to be more negative than the reduction potential of H^+/H_2 to reduce protons, and the valence band edge has to be more positive than the H_2O/O_2 redox potential to oxidize water [4].

Layered perovskite materials, like Dion-Jacobson phase niobium oxides $AB_2Nb_3O_{10}$ ($A = K, Rb, Cs$ and $B = Ca, Sr$) are known for their high photocatalytic activity under UV light irradiation [5–10]. Other properties of this group of materials include superconductivity, dielectric behavior, good electron conductivity, photoluminescence and the possibility of easy ion exchange [5–10]. Their structure consists of negatively charged niobium oxide sheets, formed by corner-sharing NbO_6 octahedra with B-cations in the

gaps between them. The positively charged A-cations are located in the interlayer space [11].

It is known that the layered structure of this type of materials is promoting the separation of photogenerated electrons and holes and thus is improving the photocatalytic activity [12]. The relatively large interlayer space allows the exchange of the A-cations by H^+ , which dramatically increases the photocatalytic activity [11]. Doping and other types of modification are also more effective compared to non-layered materials. This is because the tunnel like interlayer gaps allowing for a better and more homogenous dopant distribution in the material [13–15].

Another advantage of the layered materials is the possibility to be exfoliated, leading to the production of two-dimensional crystals, also known as “nanosheets”. Concerning the photocatalytic activity, the superiority of “nanosheets” compared to the corresponding bulk materials has been already reported [15–17].

Layered Dion-Jacobson niobium oxides are conventionally prepared by the solid state reaction [9]. The synthesis by the polymerizable complex (PC) method is also known [18]. The disadvantages of these methods are the high reaction temperatures, the exceedingly long reaction times, and the necessity of adding an excess of the A-cation precursor, due to its high volatility during the synthesis process [19,20]. Thus, such methods are unsuitable for industrial application. This work presents the molten salt method as a much more attractive synthesis process for this group of materials.

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The molten salt method has been previously utilized for the preparation of the calcium tantalate composite photocatalysts and tetragonal tungsten bronze-type nanorods [21,22]. A salt (in our case chlorides) with a lower melting temperature than that of the precursors is added in excess, acting as a solvent. In this respect, the molten salt method differs from the flux method, where the salt is added in a low amount (a few percent of the total weight) in order to enhance the reaction rate. The role of the molten salt is to lower the reaction temperature, increase the reaction rate and the homogeneity of the reaction mixture, as well as to control the particle size, shape and agglomeration rate [23].

We herein report for the first time the successful application of this method for the preparation of the family of layered Dion-Jacobson perovskite type materials $AB_2Nb_3O_{10}$ ($A=K, Rb, Cs$ and $B=Ca, Sr, Ba$). The physical properties of the compounds synthesized in this manner, as well as their photocatalytic activity for hydrogen production will be presented, the latter being strongly influenced by interlayer spacing and lattice relaxation.

2. Experimental

2.1. Reagents and materials

All chemicals were of analytical grade and used as received. $BaCO_3$ (Alfa Aesar, 99.9%), $CaCO_3$ (Gruessing, 99.0%), $CsCl$ (Alfa Aesar, 99.9%), Cs_2CO_3 (Alfa Aesar, 99.9%), KCl (Gruessing, 99.0%), K_2CO_3 (Grüssing, 99.0%), methanol (J.T. Baker, a. g.), Na_3RhCl_6 (Sigma-Aldrich, 99.9%), Nb_2O_5 (Fluka, 99.9%), perchloric acid (Sigma-Aldrich, 70%), $RbCl$ (Acros Organics, 99.9%), Rb_2CO_3 (Sigma-Aldrich, 99.8%), $SrCO_3$ (Gruessing, 99.0%), $Sr(NO_3)_2$ (Acros Organics, 99.9%)

2.2. Catalysts preparation

As shown schematically in Fig. S1 (Supplementary data), the $AB_2Nb_3O_{10}$ compounds were prepared *via* molten salt method by mixing BCO_3 or $B(NO_3)_2$, ($B=Ca, Sr, Ba$), Nb_2O_5 , A_2CO_3 with ACl ($A=K, Rb, Cs$) at a weight ratio 1:2 and heating the mixture in an alumina crucible at a compound specific reaction temperature (Table 1) for 2 h, using a Carbolite CWF 1300 muffle furnace. The obtained product was washed several times with distilled water and dried at 100 °C overnight. About 65% of the A-cation chlorides (ACl) could be recovered out of the washing water.

The compound $A=Rb$ and $B=Ba$ was also synthesized. However, since the impurity phases still dominate the product, it was left out of the following discussion. The synthesis of the compound $A=K$ and $B=Ba$ was not successful with this method.

2.3. Characterization

X-ray diffraction patterns were measured on a PANalytical MPD diffractometer using $Cu-K\alpha$ radiation ($\lambda=0.1541$ nm) in the 2θ range from 5° to 55°. The phase purity was confirmed using the HighScore Plus software version 3.0e (3.0.5) and the ICSD database ($CsCa_2Nb_3O_{10}$ 98-020-1425 [24], $CsSr_2Nb_3O_{10}$ 98-009-3675 [7],

$CsBa_2Nb_3O_{10}$ 98-009-3676 [7], $RbCa_2Nb_3O_{10}$ 98-026-0289 [25], $RbSr_2Nb_3O_{10}$ 98-009-3674 [26], $KCa_2Nb_3O_{10}$ 98-009-1098 [27]). The phase purity of $KSr_2Nb_3O_{10}$ was confirmed by comparing the XRD pattern of the compound with the current literature [28]. Raman spectra were acquired on a SENTERRA dispersive Raman microscope from Bruker Optics equipped with an Olympus (MPlanN 50x) objective and a Nd:YAG laser ($\lambda=532$ nm, $P=2.0$ mW). Scanning electron microscopy (SEM) images were recorded on a Philips LEO Gemini 982 field emission SEM at an operating voltage of 3 kV. The EDX elemental analysis was conducted on the same instrument at 20 kV accelerating voltage. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were performed on a Philips CM30 with 300 kV acceleration voltage and carbon-filmed copper mesh grids for sample preparation. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA 409 PC/PG instrument using an Al_2O_3 crucible under the following conditions: 30 mL/min. Ar gas flow, temperature range between 25 °C and 1000 °C. BET measurements were conducted on a Quantachrome Quadrasorb evo instrument at the temperature of liquid nitrogen (−196 °C). UV–vis diffuse reflectance measurements were performed on a Perkin Elmer Lambda 750 spectrometer equipped with a Praying-Mantis accessory. The reflectance spectra were recorded between 200 and 500 nm using $BaSO_4$ as reference.

2.4. Hydrogen production—experimental setup and procedure

The photocatalytic hydrogen production using the synthesized materials was performed in a double-walled inner irradiation-type quartz reactor connected to a homemade closed gas evolution system (Fig. S2 Supplementary data).

To prevent any thermal catalytic effect, the reactor was cooled down to 10 °C using a double walled quartz jacket, through which cooling water was circulated from a thermostat (Lauda). A 350 W Hg immersion lamp (UV-Consulting, Pechl) was used as light source. High purity argon was used as the carrier gas for the reaction products. The flow rate was set at 25 mL/min. and controlled by a Bronkhorst mass flow controller. The evolved hydrogen was detected using a Shimadzu GC-2014 gas chromatograph equipped with a thermal conductivity (TCD) detector and RESTEK ShinCarbon ST 100/120 column. The column was kept at 35 °C throughout the measurement. The elution time for H_2 was 1 min.

In a typical experiment 0.3 g photocatalyst was suspended (under sonication) in 600 mL aqueous methanol (10 % v/v) solution. The solution initial pH was adjusted to 5 with perchloric acid. Prior to irradiation the system was purged with argon at 100 mL/min to ensure complete air removal. The reaction was allowed to proceed for two hours without co-catalyst. After that, Rh was in-situ photodeposited (0.05 wt.-% Rh loading) on the catalyst from Na_3RhCl_6 (1.7 mL) introduced in the system with a syringe through a reactor inlet and rubber sealing (Fig. S2 Supplementary data). This procedure has the advantage that the reactor does not have to be opened, reducing the flushing time to remove air after precursor addition. Afterwards, the irradiation continued for another five hours, with a short induction period in H_2 generation due to Rh photodeposition.

Table 1
Compound specific precursors and reaction temperatures.

Compound	A Precursor	B Precursor	ACl	Weight ratio (precursors:ACl)	Temperature
$CsCa_2Nb_3O_{10}$	$CsCO_3$	$CaCO_3$	$CsCl$	1:2	750 °C
$CsSr_2Nb_3O_{10}$	$CsCO_3$	$Sr(NO_3)_2$	$CsCl$	1:2	1000 °C
$CsBa_2Nb_3O_{10}$	$CsCO_3$	$BaCO_3$	$CsCl$	1:2	850 °C
$RbCa_2Nb_3O_{10}$	$RbCO_3$	$CaCO_3$	$RbCl$	1:2	900 °C
$RbSr_2Nb_3O_{10}$	$RbCO_3$	$Sr(NO_3)_2$	$RbCl$	1:2	900 °C
$KCa_2Nb_3O_{10}$	KCO_3	$CaCO_3$	KCl	1:2	1000 °C
$KSr_2Nb_3O_{10}$	KCO_3	$SrCO_3$	KCl	1:2	1200 °C

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