Hydrothermal Single Crystal Growth and Characterization of Novel Rare Earth Niobates and Tantalates: LnNbO$_4$ (Ln = La-Lu, Y), La$_2$TaO$_5$(OH) and Ln$_3$Ta$_2$O$_9$(OH)

Liurukara D. Sanjeewa  
Clemson University

Kyle Fulle  
Clemson University

Colin D. McMillen  
Clemson University

Joseph W. Kolis  
Clemson University

Follow this and additional works at: https://tigerprints.clemson.edu/cars

Part of the Chemistry Commons

Recommended Citation
https://tigerprints.clemson.edu/cars/1

This Poster is brought to you for free and open access by the Student Works at TigerPrints. It has been accepted for inclusion in Chemistry Annual Research Symposium by an authorized administrator of TigerPrints. For more information, please contact kokeef@clemson.edu.
Hydrothermal Single Crystal Growth and Characterization of Novel Rare Earth Niobates and Tantalates: LnNbO₄ (Ln = La-Lu, Y), La₂Ta₂O₄(OH) and Ln₃Ta₂O₉(OH)

Liluarka D. Sanjeeva,1 Kyle Fulle,1 Colin D. McMullen1, Joseph W. Kelso1

1Department of Chemistry and Center for Optical Materials Science and Engineering Technologies (COMSET), Clemson University, Clemson, South Carolina 29634-0973, USA

Introduction

Rare-earth niobates and tantalates are refractory materials that have been exploited in applications involving ion conductivity, photo-catalysis, and luminescence, both in doped and undoped forms.

In general, refractory oxides have high melting points therefore synthesis of single crystals are more challenging. For example LnNbO₄ can be grown readily by melt techniques such as Czochralski pulling around 1300 °C. However during the cooling crystal quality degraded resulting in poor quality single crystals while high temperature melting techniques are not suitable for bulk crystals of tantalates.

Development of alternative synthetic methods is one promising approach to realizing the full potential of the fundamental science and application of these materials.

Of particular significance is the fact that the high temperature hydrothermal technique provide ability to grow high quality single crystals at relatively low temperatures (500-700 °C and 1-3 kbar).

Further, our group has been proved that the high temperature hydrothermal technique can be utilized with exceptionally reactive fluids under extreme conditions of temperature and pressure.

As a significant breakthrough, we recently found that the use of extremely concentrated hydroxide solutions (30-40 M KOH) and fluorides (20-30 M CsF) allow us to solubilize most refractory oxides such as ThO₂, HfO₂, ZrO₂, Nb₂O₅ and Ta₂O₅.

Use of these methods allowed us not only to explore new phase rapidly and prepare interesting new materials, but we can also grow high quality single crystals that are large enough to use in real world applications.

This demonstration mainly concentrated on the high temperature hydrothermal synthesis of single crystals and structure characterization of rare earth niobates and tantalates.

Synthesis and Structure Characterization

Single Crystal Growth

<table>
<thead>
<tr>
<th>La₂O₃</th>
<th>X₂O₃</th>
<th>with 30 M KOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>Lu, Y</td>
<td>Nd, Tb</td>
</tr>
</tbody>
</table>

All the reactions were performed in silver ampoules (3/8" x 3") containing 8 1/2 mL of 30 M KOH. All the reactions were welded into silver ampoules with 8 1/2 mL of 30 M KOH.

The autoclave was affixed with ceramic band heaters and heated to a constant temperature of 700 °C. To a constant temperature of 700 °C. The autoclave was charged with composition shown in Table. All the reactions were performed in silver ampoule (3/8" x 3") containing 8 1/2 mL of 30 M KOH.

Ampoules were weld-sealed and loaded into a 718 Inconel refractory oxides such as ThO₂, HfO₂, ZrO₂, Nb₂O₅ and Ta₂O₅.

All the reactions were performed in silver ampoules (3/8" x 3") containing 8 1/2 mL of 30 M KOH. All the reactions were performed in silver ampoules containing 8 1/2 mL of 30 M KOH.

Ampoules were weld-sealed and loaded into a 718 Inconel autoclave with a 75% fill of DI water to serve as the desired counter-pressure.

The autoclave was affixed with ceramic band heaters and heated to a constant temperature of 700 °C. To a constant temperature of 700 °C. The autoclave was charged with composition shown in Table. All the reactions were performed in silver ampoule (3/8" x 3") containing 8 1/2 mL of 30 M KOH.

Ampoules were weld-sealed and loaded into a 718 Inconel autoclave with a 75% fill of DI water to serve as the desired counter-pressure.

Further work will test to whether the hydrothermal crystal growth concepts demonstrated in this study can be extended to other refractory oxides with high temperature phase transitions, including ferroelectric or ferromagnetic materials.

Conclusion

In this study we demonstrate that the rare earth niobates and tantalates can be grown as large high quality single crystals by employing the hydrothermal technique at extreme temperatures (650 - 700 °C) using extreme alkali hydroxide solutions (30 M KOH).

This technique often resulted 1-3 mm size crystals with good quality for potential of optical applications.

Further work confirm that the hydrothermal technique can be used to separate low temperature REMO₆ (RE = Y, La) phase which crystallize in the space group of C2/c (750 °C) from its high temperature tetragonal phase RH₂O₆ (400 °C).

The preparation of lanthanide doped single crystals of the VMO₆ phase was also achieved, and the study of their optical properties is ongoing.

Additionally, use of similar technique with tantalum oxide (Ta₂O₅) with rare earth oxide was fruitful, resulting two series of novel rare earth tantalate structures, Ln₂Ta₂O₇(OH) and La₂Ta₂O₇(OH).

The compositions and structural differences in Ln₂Ta₂O₇(OH) and La₂Ta₂O₇(OH) provide an excellent example of the ability of Ta⁶⁺ to form different RE-Ta₂O₇ lattices.

Furthermore, the synthesis of new rare earth tantalates explore the possibility of synthesizing new materials targeting photocatalysts, host lattices for phosphors, and in conductors.

Finally, future work will test to whether the hydrothermal crystal growth concepts demonstrated in this study can be extended to other refractory oxides with high temperature phase transitions, including ferroelectric or ferromagnetic materials.

Acknowledgements

We are indebted to the Department of Energy Basic Energy Sciences Award Number DE-SC0014271 for support of this work. Purchase of the Bruker single crystal diffractometer was enabled by an internal grant from the office of the Clemson University Vice President for Research.

References