OFFICE OF NAVAL RESEARCH

Contract #N00014-99-1-0538

R&T Code -
PR Number 01PR01106-00
Dr. Richard T. Carlin

Technical Report # 1

"New Protonated and Anhydrous Chalcogenide Glasses"

by
Annamalai Karthikeyan, Chad A. Martindale and Steve W. Martin

Presented at the Gordon Research Conference on

"Fuel-Cells 2001", Bristol, Rhode Island.

Department of Materials Science and Engineering
Iowa State University of Science and Technology
Ames, IA 50011, USA

September 25, 2001

Reproduction in whole or in part is permitted for any purpose of the United States
Government

This document has been approved for public release and sale; its distribution is unlimited
7. Professor Steve W. Martin  
Department of Materials Science and Engineering  
Iowa State University of Science and Technology  
Ames, IA 50011, USA

8. Technical Report # 1

9. Office of Naval Research  
800 North Quincy Street  
Arlington, VA 22217


12. Reproduction in whole or in part is permitted for any purpose of the United States Government. This document has been approved for public release and sale; its distribution is unlimited.

13. Abstract:

While hydrated electrolytes exhibit high proton conductivities, their use is limited by significant methanol cross-over, mechanical stability and temperatures below 100°C. These limitations can be overcome by synthesizing anhydrous proton conducting materials. In this direction we are investigating the development of anhydrous proton conductors. Protonated (and anhydrous) chalcogenide glass and glass-ceramic materials have been prepared for the first time. These materials open a new choice for the development of fast proton conducting (FPC) electrolytes intended for electrochemical applications, fuel cells in particular. These FPC materials, with proper addition of dopants, are expected to have high proton motion and better thermal stability than polymeric electrolytes.

The protonated materials were prepared in three steps. First B$_2$S$_3$ glass was prepared from the elements. A B$_2$S$_3$ melt was bubbled with H$_2$S(g) and thioboric acid crystals (HBS$_2$) were obtained. Finally, HBS$_2$ was used as a precursor for the preparation of different glass and glass-ceramic materials, of varying compositions, by adding (i) B$_2$S$_3$/GeS$_2$.

14. Subject terms: new protonated glasses, thioboric acids, preparation, IR, Raman, NMR.

15. No. of pages:

16. Price code:

17. Unclassified:
New Protonated and Anhydrous Chalcogenide Glasses
Annalalai Karthikeyan, Chad A. Martindale, Steve W. Martin

MOTIVATION
Hydrated electrolytes have limited applications above 100°C and problems of methanol cross-over and mechanical stability occur. Anhydrous proton conducting materials can overcome these problems. Chalcogenide glasses are promising host materials for fast proton conduction (FPC). We are investigating:
(i) Preparation of anhydrous protonated chalcogenide glassy materials.
(ii) Achieving FPC in these materials with good thermal stability.
(iii) Fuel cell development based on these anhydrous-FPC materials.

PREPARATION
(i) 2B + 3S → B₂S₃ (glass) - at 850 °C for 12 hrs in sealed carbon-coated silica tube.
(ii) (3/2)B₂S₃ + (3/2)H₂S → (HBS₃)₂ - (crystalline)
- H₂S gas bubbled in B₂S₃ melt (at 500 °C with a H₂S flow of ~ 6 ml/min) and the condensed vapor (HBS₃)₂ collected.
-This is a new method to prepare (HBS₃)₂ and only requires lower temperatures.

IR and Raman Spectra of (HBS₃)₂
Trimer Units (HBS₂)₃
6-membered rings

(iii) (a) HBS₂ + B₂S₃ → H₂S+B₂S₃ (glass & glass-ceramics).
(b) HBS₂ + GeS₂ → H₂S+B₂S₃+GeS₂ (glass-ceramics).
(c) HBS₂ + S → H₂B₂S₃ - (ceramics)

Fine powders of starting materials were mixed and sealed under vacuum in a silica tube. The sealed tube was heated to 300 °C to 550 °C. Glasses and glass-ceramic samples were obtained by quenching the melt in the silica tube.

IR Spectra: (HBS₂ + B₂S₃) (HBS₂ + GeS₂)

¹H-NMR Spectra

¹¹B-NMR Spectra

DISCUSSIONS
The H-S bonding in the IR spectra signifies the presence of protons in the materials. The 6-membered-ring modes (1000cm⁻¹), are also observed in the protonated glasses. The trigonal modes (800 cm⁻¹), are present in all the samples. This indicates that no trigonal to tetrahedral conversion occurs in the samples with the addition of H₂S. The 6-membered-ring modes, weaken upon addition of GeS₂. Higher H₂S concentration are achieved by adding GeS₂.

¹H-NMR confirms the presence of protons in the glass and glass-ceramic materials. The ¹¹B-NMR shows a resonance peak corresponding to trigonal coordination in all samples, as in IR.

CONCLUSIONS
New anhydrous protonated glassy materials have been prepared. The present materials opens a new choice for glass-ceramic research. These materials with suitable modifications are expected to have good proton conduction and better thermal stability. They may be better alternatives for conventional hydrous proton conducting materials.

Acknowledgements: Funding from Office of Naval Research (ONR): Award Number – N00014-99-1-0538. Special thanks to Ben Meyer for NMR measurements.