

# Microscopic structure of tin-borate and tin-boratephosphate glasses

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## Abstract

The structure of tin-borate and tin-boratephosphate glasses has been examined with diffuse reflectance infrared (DR-IR) and Raman spectroscopy. The basic network structure for these glasses is described as well as the positioning of tin in the network. Data suggests that the amount of phosphate present in the glass regulate the glass forming properties of tin. With borate as the dominating glass forming oxide, SnO acts like a glass former, but with increasing amount of phosphate SnO instead tends to behave as a network modifier.

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## 1. Introduction

Today's society with its technological development of portable computers, entertainment and telecommunication equipment gives rise to a rapidly increasing demand for portable and effective energy sources. The key component is the rechargeable Li-ion cell and the demand has pushed the development of new and improved materials for electrolytes and electrode materials (for a recent review see [1]). On the negative electrode side, one is searching for alternatives to carbon electrodes in order to find materials with higher capacity and more positive intercalation voltages. One of the new kinds of promising materials are tin composite oxide (TCO)-based glasses [2]. Despite its high capacity and good cycle-ability it suffers from a major drawback with the large amount of irreversible capacity lost during the first cycle. Many attempts [3–9] have been made to explain the mechanism behind the lithium insertion/extraction process for this material. Knowledge of the mechanism should then also reveal some explanation for the cause of the detrimental capacity loss.

Earlier studies [6–9] have shown that the glass network structure affects the lithium insertion process. Since the original TCO glass contained many different compounds, simplified glasses, such as Sn<sub>2</sub>BPO<sub>6</sub>, Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub>, have been examined to characterise the importance of each compound. These studies [8,9] have shown that certain glass forming

oxides have a higher resistance towards disruptive and irreversible reactions occurring when lithium enters the glass electrode. Since these reactions make up a major part of the capacity loss they should be minimised.

In this work, we have focused on investigating the microscopic structure of some different tin borate and tin-boratephosphate glasses using vibrational spectroscopy and neutron diffraction. Information of the local tin environment as well as the network structure in these glasses is of vital importance for the understanding of their electrochemical cycling performance.

## 2. Experimental

The glasses were made by mixing appropriate amounts of SnO, B<sub>2</sub>O<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub> and Sn<sub>2</sub>P<sub>2</sub>O<sub>7</sub> to form the following compositions: SnB<sub>0.3</sub>P<sub>0.9</sub>O<sub>3.7</sub>, SnB<sub>0.6</sub>P<sub>0.5</sub>O<sub>3.2</sub>, SnB<sub>0.9</sub>P<sub>0.5</sub>O<sub>3.6</sub>, SnB<sub>1.3</sub>P<sub>0.2</sub>Al<sub>0.5</sub>O<sub>4.2</sub> and SnB<sub>2.2</sub>O<sub>4.3</sub>. The ground mixtures were heated in graphite crucibles under Ar-atmosphere to 1000 °C for at least 6 h. The mixtures were then quenched onto a copper plate at room temperature. The amorphous state was confirmed using X-ray diffraction and an ICP analysis was performed on the glasses as to ensure the ratio between tin, boron, phosphorous and aluminium.

Diffuse reflectance infrared (DR-IR) spectra were collected using a Bruker IFS 66v/s FT-IR spectrometer, equipped with exchangeable mercury–cadmium–telluride (MCT) and deuterated triglycerine sulfate (DTGS) detectors and a diffuse reflectance device (Graseby Specac, Mod. Selector). The resolution was 4 cm<sup>-1</sup> and 200 scans were

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accumulated for each spectrum in the range 80–2000  $\text{cm}^{-1}$ . The diffuse reflectance from a wrinkled aluminium surface was used as reference. The data were treated by taking the ratio of the reflected intensity from the glass to that from the reference.

The Raman scattering experiments were performed on a Dilor XY800 spectrometer equipped with an  $l\text{-N}_2$  cooled CCD detector. The 514.5 nm  $\text{Ar}^+$  ion laser line was used for excitation of the samples. A confocal microscope, Olympus BH-2 with a 100 $\times$  objective, was used for focusing the incoming beam and collecting the scattered light. The investigated spectral range was 30–2000  $\text{cm}^{-1}$ .

### 3. Results and discussion

#### 3.1. Diffuse reflectance infrared spectroscopy

The results from the diffuse reflectance measurements for the investigated glasses are shown in Fig. 1. The investigated spectral range provides mainly information about the borate and boratephosphate network. For example, the absorption in the 800–1150  $\text{cm}^{-1}$  range can be attributed to four co-ordinated boron while bands in the 1150–1550  $\text{cm}^{-1}$  region are associated to three co-ordinated boron.

For the  $\text{SnB}_{2.2}\text{O}_{4.3}$  glass vibrational bands associated with three co-ordinated boron dominate the high frequency part of the spectrum (see Fig. 1). Due to the large amount of SnO present in the glass the boron is expected to have one or more non-bridging oxygen. A band at 1490  $\text{cm}^{-1}$ , usually assigned to  $\text{B-O}^-$  vibrations in larger borate units, supports this assumption. The band at 1290  $\text{cm}^{-1}$  can be attributed to vibrations in methaborate chains and the band at 1110  $\text{cm}^{-1}$  to smaller borate units such as pyroborate. The band at 720  $\text{cm}^{-1}$  is associated with  $\text{B-O-B}$  vibrations, probably in

the methaborate chain. Thus, for the  $\text{SnB}_{2.2}\text{O}_{4.3}$  glass we conclude that it is mainly methaborate groups that build up the network.

The spectrum of the borate phosphate glass with the smallest addition of phosphate (and with additional aluminium),  $\text{SnB}_{1.3}\text{P}_{0.2}\text{Al}_{0.5}\text{O}_{4.2}$ , shows that the main methaborate structure is preserved. The vibrational bands of the methaborate groups are however somewhat shifted due to the presence of phosphate and aluminium. Since there is only a slight change of the peaks, aluminium should not be a part in the main network, but is instead dispersed between the chains.

On further addition of phosphate (now without aluminium), the spectrum of  $\text{SnB}_{0.9}\text{P}_{0.5}\text{O}_{3.7}$  shows a peak at 1150  $\text{cm}^{-1}$  that can be assigned to  $\text{P-O}^-$  vibrations in the orthophosphate group, while the peaks due to  $\text{B-O}^-$  and  $\text{B-O-B}$  vibrations are shifted to lower wave-numbers. This trend continues for addition of more phosphate, i.e. for  $\text{SnB}_{0.6}\text{P}_{0.5}\text{O}_{3.2}$  and of  $\text{SnB}_{0.3}\text{P}_{0.9}\text{O}_{3.7}$ . However, for the  $\text{SnB}_{0.3}\text{P}_{0.9}\text{O}_{3.7}$  glass, the peak due to  $\text{P-O}^-$  vibrations is shifted to higher frequencies and increases in intensity. This resembles vibrations due to pyrophosphate instead, which is supported by the appearance of the peak at 750  $\text{cm}^{-1}$  that is attributed to  $\text{P-O-P}$  vibrations.

From the spectra it can thus be concluded that the borate part of the network mainly form methaborate chains and with small addition of phosphate the phosphate form orthophosphate groups. Further addition of phosphate disturbs the methaborate chain slightly and the phosphate starts to form larger phosphate units such as pyrophosphate.

#### 3.2. Raman spectroscopy

In Fig. 2, we show the Raman spectra taken for the investigated glasses. Again we compare the spectrum of

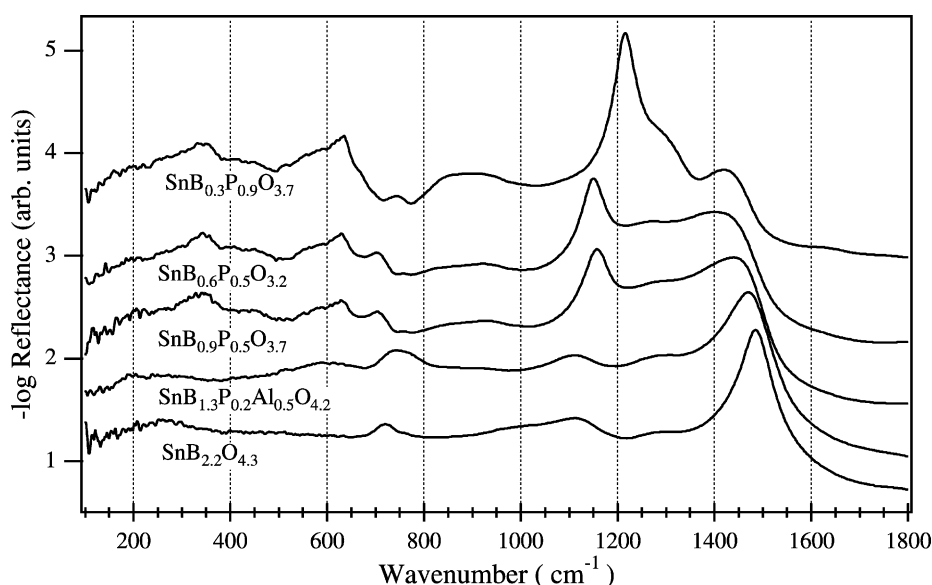


Fig. 1. DR-IR spectra of the different tin-borate and borate phosphate glasses.

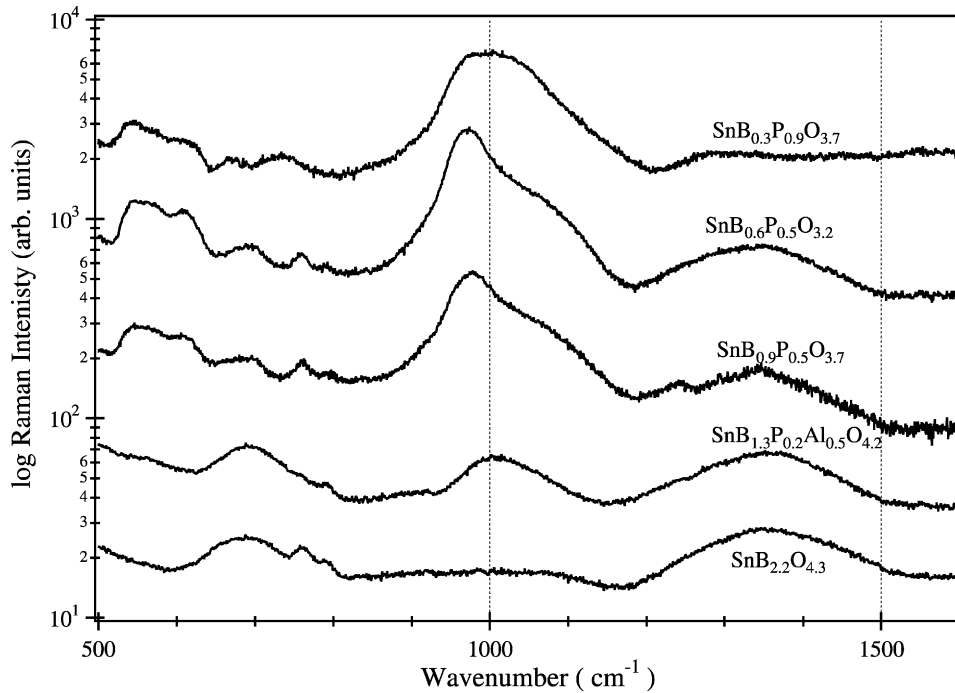


Fig. 2. Raman spectra of the different tin-borate and tin-boratephosphate glasses.

the tin-borate glass  $\text{SnB}_{2.2}\text{O}_{4.3}$  with those of the glasses with increasing phosphate content. In the spectrum for the  $\text{SnB}_{2.2}\text{O}_{4.3}$  glass we note that the bands at 1330 and  $700\text{ cm}^{-1}$  can be assigned to vibrations of methaborate groups. On addition of phosphate and aluminium these are preserved and a new band at around  $1000\text{ cm}^{-1}$  also

arises. This band can be assigned to small phosphate units as pyrophosphate or orthophosphate.

For the  $\text{SnB}_{0.9}\text{P}_{0.5}\text{O}_{3.7}$  glass (see Fig. 2), the band associated with orthophosphate and pyrophosphate units has increased markedly in intensity relative to that of the methaborate band. There is also a change of the B–O–B

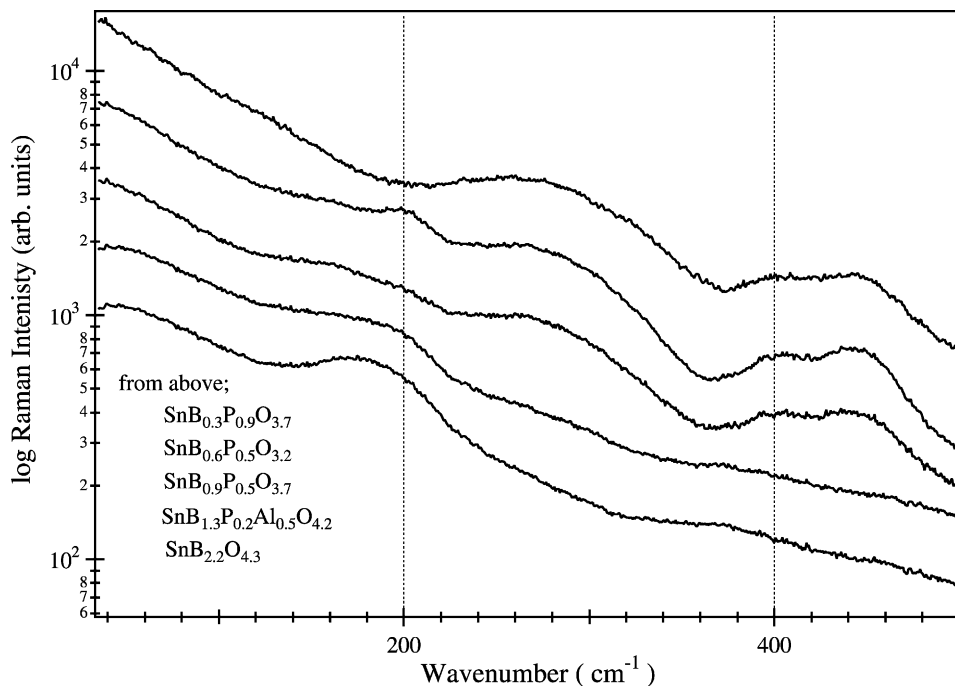


Fig. 3. Low frequency Raman spectra of the different glasses.

band around  $700\text{ cm}^{-1}$  and a band has arisen at  $760\text{ cm}^{-1}$  that indicates some variations in the length of the methaborate chains, probably due to incorporation of phosphate units. The trend on further addition of phosphate is an increase of the intensity of orthophosphate vibrations ( $950\text{ cm}^{-1}$ ) and even some evidence of pyrophosphate ( $1050\text{ cm}^{-1}$ ) along with a shortening of the methaborate chain. When reaching the  $\text{SnB}_{0.3}\text{P}_{0.9}\text{O}_{3.7}$  glass composition, the spectrum shows that the methaborate units have decreased significantly in favour for the pyrophosphate and orthophosphate units. There are also indications of some shorter borate units as orthoborate/pyroborate with a peak at  $1270\text{ cm}^{-1}$ . The shape of the peak at  $1000\text{ cm}^{-1}$  changes and it seems that the amount of pyrophosphate now is dominating over the *ortho* composition. The conclusions of the Raman study about the structures of the glasses agree well with the results of the infrared spectroscopy investigation (see above).

Specific information regarding the role of the tin in these glasses can be obtained from the Raman spectral region below  $500\text{ cm}^{-1}$ , displayed in Fig. 3. In this regions, we see several changes of the spectra for increasing phosphate content, e.g. in the regions around  $200$ ,  $270\text{ cm}^{-1}$ . We may consider using crystalline stannous oxide (c-SnO) as a reference. With its Raman spectrum presenting two sharp peaks at  $166$  and  $206\text{ cm}^{-1}$  [8], we can associate a network forming behaviour to tin compounds showing metal-oxygen vibrations at such frequencies. In the  $\text{SnB}_{2.2}\text{O}_{4.3}$  glass there is a large band present at  $175\text{ cm}^{-1}$  that can be associated with Sn–O vibrations. This band is slightly broader for the  $\text{SnB}_{1.3}\text{P}_{0.2}\text{Al}_{0.5}\text{O}_{4.2}$  glass and a second component seems to grow at around  $200\text{ cm}^{-1}$ . These bands, although much broader and slightly shifted, resemble rather well the peaks observed in Raman spectra of c-SnO.

With further addition of phosphate another band at  $270\text{ cm}^{-1}$  is arising which can be related to other Sn–O vibrations. This band tends to become more important with respect to the other two, with an increase of the phosphate content in the glass. Finally, for the  $\text{SnB}_{0.3}\text{B}_{0.9}\text{O}_{3.7}$  glass there is only the band at  $270\text{ cm}^{-1}$  present. The apparent observation is that the co-ordinations of tin gradually changes for increasing phosphate content in the glasses. It is thus possible that the tin is mostly associated with a phosphate environment in a borate phosphate glass with high amount of phosphate. The trend may also suggest that tin is incorporated in the network as a network former in the methaborate glass, while it assumes more and more the role of a modifier with the increase of phosphate in the glass. It is then the amount of phosphate present in the glass that regulates the role of tin in the glass from a glass former to a modifier of the network structure.

### 3.3. Reverse Monte Carlo modelling

A reverse Monte Carlo (RMC) simulation of the  $\text{SnB}_{2.2}\text{O}_{4.3}$  glass, using experimental neutron diffraction data,

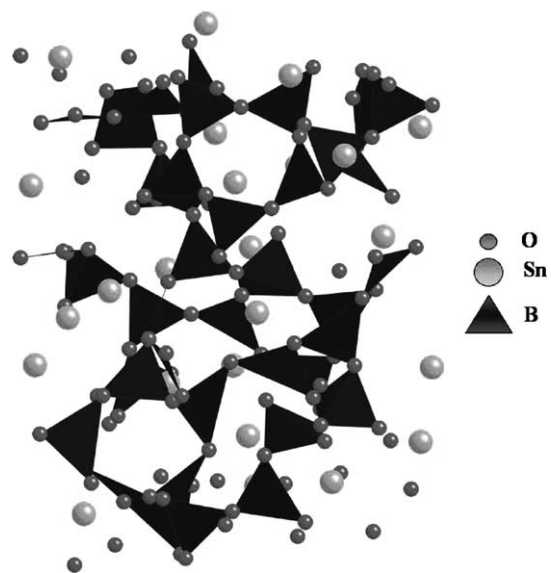


Fig. 4. Structure of a tin-oxide borate glass obtained from a RMC simulation on neutron diffraction data. The figure shows a ( $7\text{ \AA} \times 10\text{ \AA} \times 10\text{ \AA}$ ) slice.

revealed a detailed 3D-model of the glass structure [10]. Fig. 4 shows a slice representing the 3D RMC model of the glass structure. From the model a probable average B–O co-ordination number of about 3.3 were obtained. This is in agreement with the present infrared and Raman measurements, which show that vibrations assigned to methaborate chains are the main features of the vibrational spectrum. The position and co-ordination of tin in the network could also be partly resolved by the RMC structural model. The model indicates that the tin atoms bridge between two neighbouring borate units and thereby that tin-oxide acts more as a network glass former than simply as network modifier. This is corroborated by the Raman data for the glass, which show vibrational bands associated with tin atoms situated in the network chains and not simply being dispersed between them.

## 4. Conclusion

The structure of a series of tin-boratephosphate glasses has been investigated by vibrational (infrared and Raman) spectroscopy. The results reveal some basic information regarding the network structure and its evolution with increasing phosphate content. For no or low phosphate content the structure consists mainly of a network of methaborate chains in which Sn acts as a glass former. For increasing phosphate content the data indicate that phosphate groups are incorporated into the network, which disrupts the methaborate chain structure, and that SnO rather acts as a network modifier with the Sn ions dispersed in between the network structure. Thus, the data shows that Sn environment is different in borate and phosphate rich glasses. A RMC model for the tin-borate glass supports the main findings spectroscopy data.

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