JOURNAL OF MATERIALS SCIENCE **35** (2000) 1695–1698

Crystallization mechanism in amorphous material of $0.5LiMnO_2$-$0.5B_2O_3$

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$0.5LiMnO_2$-$0.5B_2O_3$ glass has been prepared by quenching a melt of $LiNO_3$, MnO_2 and B_2O_3 at 1100°C to room temperature in air. The crystallization mechanism of this kind of glass was investigated by differential thermal analysis (DTA) and powder X-ray diffraction (XRD). It is shown that the substances crystallized from powder and bulk samples are different because manganese with lower valence in powder sample can be further oxidized by the oxygen penetrated through the large surface of powder sample. For a powder sample the glass transition endothermic peak in the DTA curve is overlapped by an exothermic reaction attributed to the oxidization of Manganese. $LiMn_2O_4$ can not be crystallized directly from the glass matrix but can be formed on the surface of glass particles by effect of oxygen in air near the glass transition temperature.

1. Introduction

Among the most promising cathode materials for lithium ion batteries, lithium manganese oxide has attracted extensive research interests in recent years. However, the cycling performance of this material is still under improvement [1]. One effective way to improve the cyclic ability of a cathode material is to vary the metal-oxygen bond lengths in the structure by using a network former [2]. Successful work has been done in framework oxides such as V_2O_5-P_2O_5 [2, 3]. In this system, framework metal oxides offer attractive characteristics, e.g., high free energy of retention, high theoretical capacities, and especially long cycle life and lower potentials without structural damage [4]. Chen and Schoonman [5] have prepared $0.3LiMn_2O_4$-$0.7B_2O_3$ glass and studied its electronic properties. They attributed the conduction of this material to the small polaron hopping. However, its crystallization process has not been studied.

In this paper, we studied the crystallization process in the $0.5LiMnO_2$-$0.5B_2O_3$ glass by differential thermal analysis and powder X-ray diffraction. To our knowledge, there has not been any report on the crystallization mechanism of lithium manganese borate oxide glass.

2. Experimental

Commercial powder reagents $LiNO_3$, MnO_2, and B_2O_3 were mixed at a molar ratio of $Li : Mn : B = 1 : 1 : 2$ and the mixture was baked at 300°C for 5 hours. The baked sample was reground and melted in an alumina crucible at 1100°C. Lithiated manganese oxide borate glass was prepared by quenching the melt between two brass plates in air. Some pieces of glass were regrounded into powder with size less than 30 μm.

Differential thermal analyzer, SETARAM TG-92, was used to study the crystallization process of the powder and as-quenched bulk samples. X-ray diffraction measurements were done on a Rigaku X-ray diffractometer with Cu K_{α_1} radiation monochromated by a graphite single crystal at 40 KV/140 mA.

3. Results and discussion

3.1. Differential thermal analyses of $0.5LiMnO_2$-$0.5B_2O_3$ glass

The DTA curves (Fig. 1) were measured by heating the $0.5LiMnO_2$-$0.5B_2O_3$ glass samples at a rate of 20°C min^{-1} in flowing air. The DTA trace for bulk sample (Fig. 1a) showed a shift change to the baseline at about 440°C. This shift was attributed to the glass transition. However, no similar change was observed in the trace for powder sample (Fig. 1b). Successively, three exothermic peaks were observed in the DTA traces of powder and bulk samples, though they are quite different in intensity and position. The first and second peaks appeared at the same positions (510–560°C) for the two traces; but the intensity of the second peak for the bulk sample was much higher than that for the powder sample. A remarkable difference was observed in the third peak. The third peak for the powder sample was very sharp in comparison with that for the bulk sample, and the peak temperature for the powder sample was 60°C lower than that for the bulk sample.

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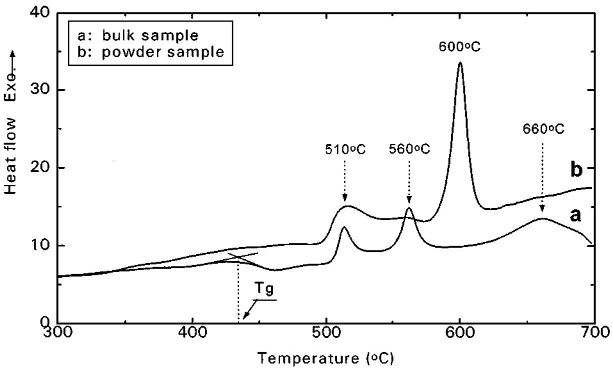

Figure 1 Different thermal analysis curves for the powder and bulk samples of 0.5$LiMnO_2$-0.5B_2O_3 glass. Heating rate: 20°C/min; atmosphere: air.

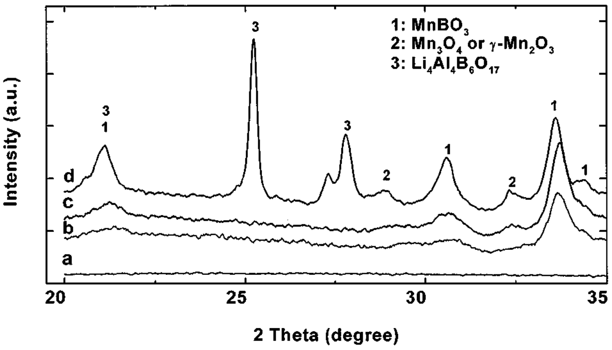

Figure 2 X-ray diffraction patterns for powder samples of 0.5$LiMnO_2$-0.5B_2O_3 glass. (a) Pristine sample; (b–d) heat treated samples after 1st, 2nd, 3rd crystallization peak respectively. The numbers of each crystalline substance are corresponding to the order of the crystallization peaks.

3.2. Crystalline substances from powder sample: $MnBO_3$, Mn_3O_4/γ-Mn_2O_3, $Li_2B_4O_7$ (or $Li_4Al_4B_6O_{17}$)

X-ray diffraction patterns of powder samples at different crystallization periods were shown in Fig. 2. Fig. 2a showed a typical XRD pattern of 0.5$LiMnO_2$-0.5B_2O_3 glass material. XRD pattern of the first crystalline substance formed at the first exothermic peak was shown in Fig. 2b. This substance was identified to be $MnBO_3$ according to the JCPDS data. The amount of this substance increased with increasing temperature as shown in Fig. 2c and d. Since the second exothermic peak in the powder DTA curve was very weak and close to the first peak, it was difficult to identify the corresponding substance secondly crystallized from the matrix. By using X-ray diffractometer with higher resolution the compound was determined as Mn_3O_4 or γ-Mn_2O_3 (the two compounds have very similar X-ray diffraction profiles). When the temperature increased further, the third exothermic peak appeared and $Li_4Al_4B_6O_{17}$ was formed as shown in Fig. 2d. The comparison of standard *d*-values of identified crystalline substances with the measured data of powder samples is showed in Table I. The element Al in the compound comes from the Al_2O_3 crucible. Al_2O_3 may be eroded by B_2O_3 and dissolved into the melt when the glass was melted in an alumna crucible at 1100°C. In order to confirm this assumption, samples with the same raw material were prepared at 1100°C for 0.5 h. and 4 h. respectively. It can be seen from Fig. 3, $Li_2B_4O_7$ crystallized from the sample with shorter soak time and no $Li_4Al_4B_6O_{17}$ was detected.

TABLE I Comparison of standard *d*-values of identified crystalline substances with the measurement data in powder samples

	Standard *d*-values (Å) of identified crystalline substances		
Measured *d*-value (Å)	$MnBO_3$ (43-59)	Mn_3O_4(24-734) or γ-Mn_2O_3(18-803)	$Li_4Al_4B_6O_{17}$ (15-344)
4.21	4.18		
3.53			3.53
3.27			
3.21			3.21
3.09		3.08	3.12
2.92	2.95		
2.77		2.77	
2.67	2.69		
2.61	2.63		
2.49		2.49	

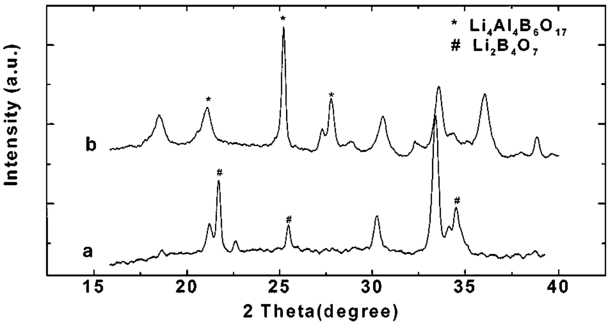

Figure 3 X-ray diffraction patterns of 0.5$LiMnO_2$-0.5B_2O_3 glass prepared in Al_2O_3 crucibles melting at 1100°C for 0.5 h. (a) and 4 h. (b), respectively.

3.3. Crystalline substances from annealing bulk sample: $MnBO_3$, $Mn(BO_2)_2$, Mn_3O_4/γ-Mn_2O_3, $Li_4Al_4B_6O_{17}$ and unknown substance

Fig. 4 shows X-ray diffraction patterns of the bulk samples annealed at different temperatures. $MnBO_3$ was crystallized firstly. When the temperature was over the second exothermic peak temperature, $Mn(BO_2)_2$ was

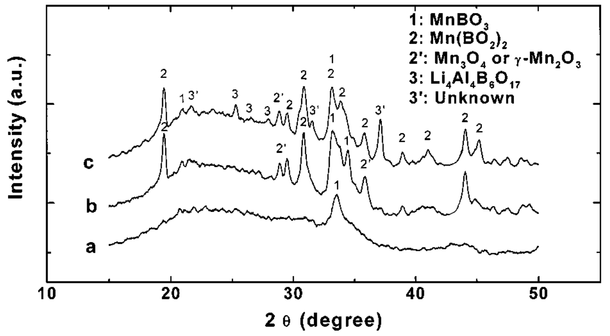

Figure 4 X-ray diffraction patterns for the bulk samples of 0.5$LiMnO_2$-0.5B_2O_3 glass when heated to the three crystallized temperature: (a) 1st (b) 2nd (c) 3rd. The number of each crystalline substance is corresponding to the order of the crystallization peaks.

crystallized from the glass matrix accompanied with a little Mn_3O_4/γ-Mn_2O_3. As can be seen from the intensity of exothermic peak on DTA trace and XRD pattern, $Mn(BO_2)_2$ is the main crystallized substance from the bulk sample where Mn is at +2 valence state. This phenomenon is quite different from that in the powder sample. The substances formed corresponding to the third mild peak can not be identified completely according to the JCPDS data. Although a little $Li_4Al_4B_6O_{17}$ can be distinguished, two lines with significant intensity leave unkown. Further work needs to confirm if it is a new substance of lithium aluminum borate oxide. The comparison of standard d-values of identified crystalline substances with the measured data of powder samples is showed in Table II.

3.4. Formation of $LiMn_2O_4$ on the surface of powder sample

The XPS results for glass are shown in Fig. 5. A satellite peak appeared at about 647 eV in the Mn $2p_{3/2}$ spectrum indicates the existence of Mn^{+2} [6, 7], and the

TABLE II Comparison of standard d-values of identified crystalline substances with the measurement data in bulk samples

	Standard d-values (Å) of identified crystalline substances				
Measured d-value (Å)	$MnBO_3$ (43-59)	Mn_3O_4(24-734) or γ-Mn_2O_3(18-803)	$Mn(BO_2)_2$ (3-0815)	$Li_4Al_4B_6O_{17}$ (15-344)	**?**
4.56			4.52		
4.25	4.24			4.27	
4.09					4.09
3.51				3.53	
3.19				3.21	
3.09		3.08		3.12	
3.03			3.04		
2.92	2.95				
2.90					
2.88		2.88	2.88		
2.84					2.84
2.70					
2.69	2.69		2.68		
2.64			2.64		
2.62	2.62				
2.58	2.59				
2.50		2.49	2.50		
2.42				2.45?	2.42
2.31			2.31		
2.20			2.18 + 2.22		
2.09	2.08				
2.06		2.04	2.04		
2.00			2.01		

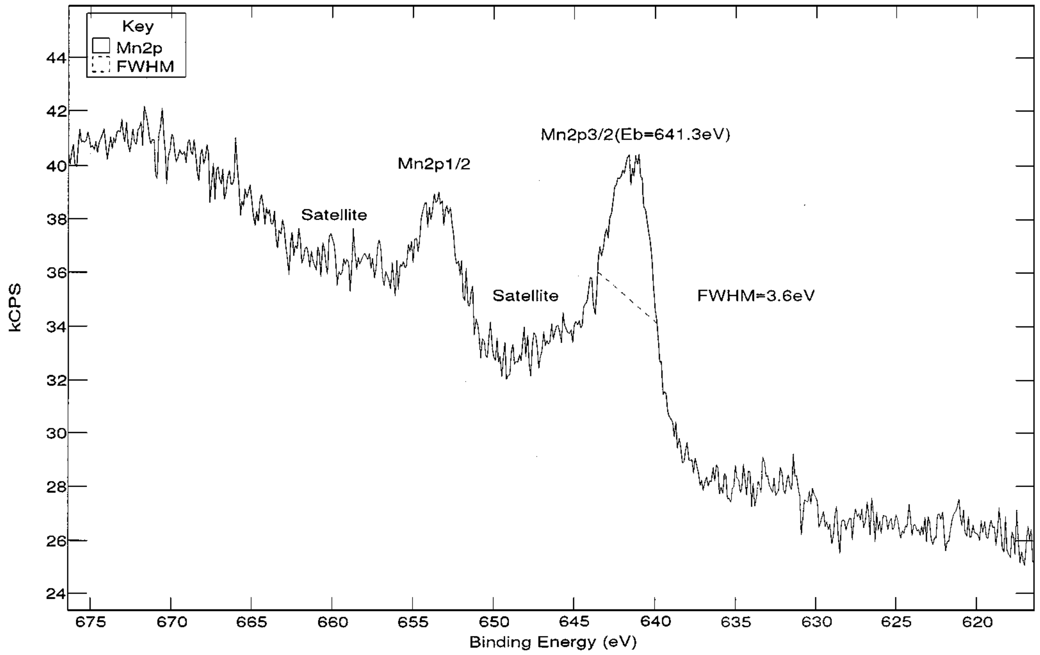

Figure 5 XPS profile of $0.5LiMnO_2$-$0.5B_2O_3$ glass.

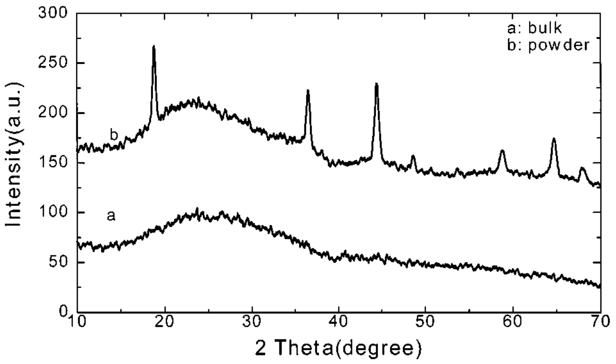

Figure 6 X-ray diffraction patterns for 0.5LiMnO$_2$-0.5B$_2$O$_3$ glass of annealed bulk sample (a) and powder sample (b).

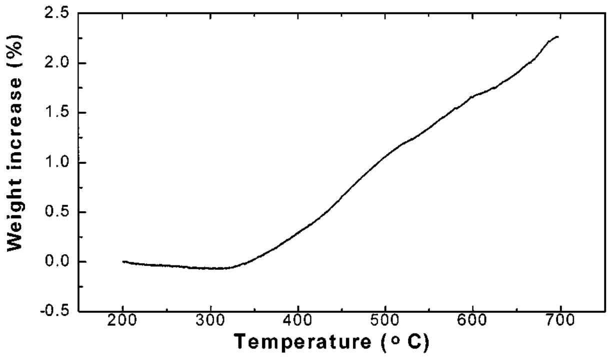

Figure 7 The TG trace for the powder sample of 0.5LiMnO$_2$-0.5B$_2$O$_3$ glass.

binding energy for Mn 2p$_{3/2}$ is 641.3 eV, quite close to 641.1 eV in MnO but far away from 642.1 eV in Mn$_2$O$_3$ [9]. It also indicates that the main valence state of Mn in 0.5LiMnO$_2$-0.5B$_2$O$_3$ glass is +2. While the majority products crystallized from powder sample is MnBO$_3$, in which manganese is occupied +3 valence state. This phenomenon was attributed to the penetration of oxygen through the surface of glass powders.

It has been mentioned that the glass transition temperature could not be observed in the DTA curve for powder sample. However, the transition temperature was obvious in the bulk sample. In order to understand the phenomenon, a powder sample and a bulk sample were heat-treated at about 400°C for elongated time. The XRD patterns for the two baked samples were shown in Fig. 6. A well-defined crystallite was formed in powder sample but no crystallite was observed in the baked bulk sample. The substance was identified to be LiMn$_2$O$_4$ [8]. The experimental show us that LiMn$_2$O$_4$ can not be directly crystallized from the glass matrix but can be formed on the surface of glass with oxygen penetration from air by annealing at glass transition temperature. Fig. 7 showed a TG curve for the powder sample. An obvious weight increase was observed from about 330°C in the TG curve. The increase of weight is evident for this oxidation reaction in the powder glass. The endothermic shift of glass transition has been overlapped by the exothermic formation reaction of LiMn$_2$O$_4$ in powder glass.

4. Conclusions

The crystallization process for 0.5LiMnO$_2$-0.5B$_2$O$_3$ glass has been studied by differential thermal analyses in a temperature range of 100°C to 700°C. Three crystallization peaks corresponded to different crystallization processes in powder and bulk samples. MnBO$_3$, Mn$_3$O$_4$/γ-Mn$_2$O$_3$, Li$_2$B$_4$O$_7$ (Li$_4$Al$_4$B$_6$O$_{17}$) were crystallized successively in the powder sample where MnBO$_3$ is the dominant manganese crystallization product; while MnBO$_3$, Mn(BO$_2$)$_2$, Mn$_3$O$_4$/γ-Mn$_2$O$_3$, Li$_4$Al$_4$B$_6$O$_{17}$ etc. were formed in the bulk sample where Mn(BO$_2$)$_2$ is the major crystalline compound. This difference should be attributed to the penetration of oxygen through the large surface of powder sample. In the meantime, an obvious weight increase observed in the Li-Mn-B-O glass system was due to the oxidation of manganese. After studying the crystalline process we suggest that manganese in Li-Mn-B-O glass is mainly in +2 valence state which is confirmed by the results of XPS. Spinel lithium manganese oxide can not be crystallized directly from the glass matrix. It was found that Spinel LiMn$_2$O$_4$ could be obtained on the surface of powder by annealing in air near the glass transition temperature.

Acknowledgements

This work was financially supported by 863 National Project (Grant No. 715-004-0280), Ford-China Foundation (Contract No. 9712304) and National Natural Science Foundation of China (No. 59672027).

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Received 28 September 1998
and accepted 28 September 1999