X-ray Structural Study of Ferromagnetic Vitreous $0.5\,La_{0.7}Sr_{0.3}MnO_3 0.5\,B_2O_3$

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The ordinary x-ray diffraction profile and the anomalous x-ray scattering profiles at Sr K-absorption edge were measured in a ferromagnetic oxide glass of $0.5La_{0.7}Sr_{0.3}MnO_3 0.5B_2O_3$. The result indicates the characteristic feature of coexistence of a highly ordered perovskite $La_{0.7}Sr_{0.3}MnO_3$-like region and a random network structure consisting of BO_3 triangles. It is expected that the characteristic magnetic properties of this sample are attributed to this distinctive structure.

Recently, a ferromagnetic oxide glass was found in the La-Sr-Mn-B-O system [1]. It is transparent, and its Curie temperature is above room temperature. It is notable that this glass may so far be the only amorphous oxide without any ferric ion. Perovskite $La_{1-x}Sr_xMnO_3$ is known to have a ferromagnetic Curie temperature above room temperature. Jonker and Van Santen [2] explained the ferromagnetic properties as the result of a strong positive Mn^{3+}-Mn^{4+} exchange interaction combined with a weak Mn^{3+}-Mn^{3+} interaction and a negative Mn^{4+}-Mn^{4+} interaction. Therefore the ferromagnetic properties of amorphous $0.5\,La_{1-x}Sr_xMnO_3 0.5\,B_2O_3$ might be explained by a similar mechanism. However, its Curie temperature shows a completely different dependence on the Sr concentration. The Curie temperature of crystalline $La_{1-x}Sr_xMnO_3$ steeply decreases with the Sr concentration above $x=0.5$ because of the increase in the negative exchange interaction of the Mn^{4+}-Mn^{4+} pairs [2]. On the other hand, the Curie temperature of $0.5La_{1-x}Sr_xMnO_3 0.5B_2O_3$ glass is almost constant above $x=0.5$ although it increases with the Sr concentration up to $x=0.5$ in a similar manner as that in the crystal. Inomata et al. [1] suggested that this distinct property results from oxygen deficiencies which may be introduced by the melt-quenching.

To the best of our knowledge, the structure of this relatively new Mn-based oxide glass has not yet been studied. This paper presents such a study by x-ray diffraction coupled with anomalous x-ray scattering.

A sample was prepared from high-grade La_2O_3, $SrCO_3$, $MnCO_3$ and B_2O_3 powders. The materials were weighed in the desired proportions and milled in water to mix them thoroughly, followed by drying and pre-firing. The product was again milled, dried and fired. The sintered body was melted by induction heating in a platinum crucible with a small nozzle of 1.0 mm diameter, and the melt was rapidly solidified by the twin-roll method so as to obtain amorphous ribbons of 10 to 30 mm length and 10 to 30 μm thickness. Details of the sample preparation are given in [1].

The x-ray scattering intensity was measured with a molybdenum x-ray target and a Ge 111 flat single crystal monochromator in an incident beam. After the corrections for absorption and polarization, the intensity was converted to electron units per atom with the generalized Krogh-Moe-Norman method [3] using the x-ray atomic scattering factors, including their anomalous dispersion terms [4], and subtracted Compton scattering [5]. The interference function, $Q\,i(Q)$, shown with a solid line in Fig. 1, was computed from this converted intensity.

By comparing this interference function with that of vitreous B_2O_3 [6, 7], it is found that the small shoulder at about 18 nm^{-1} on the low-Q side of the first peak corresponds to the first peak in the B_2O_3 glass. Thus

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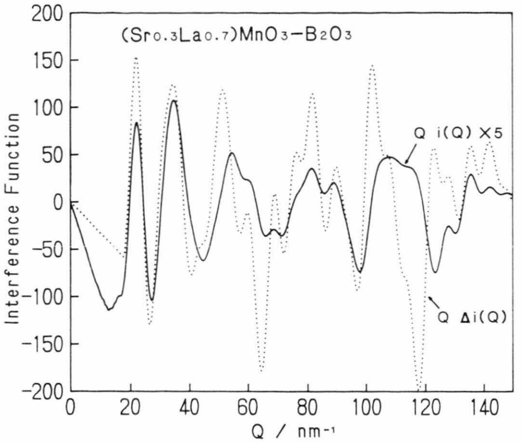

Fig. 1. Interference functions $Q\,i(Q)$ (solid line) and $Q\,\Delta i(Q)$ (dotted line) in vitreous $0.5\,La_{1-x}Sr_xMnO_3 0.5\,B_2O_3$

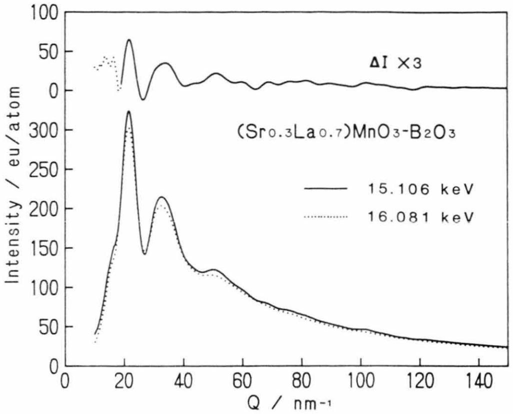

Fig. 3. Intensities measured at 15.106 and 16.081 keV below the Sr K-absorption edge (16.106 keV) and the difference between them (top) in vitreous $0.5\,La_{1-x}Sr_xMnO_3 0.5\,B_2O_3$

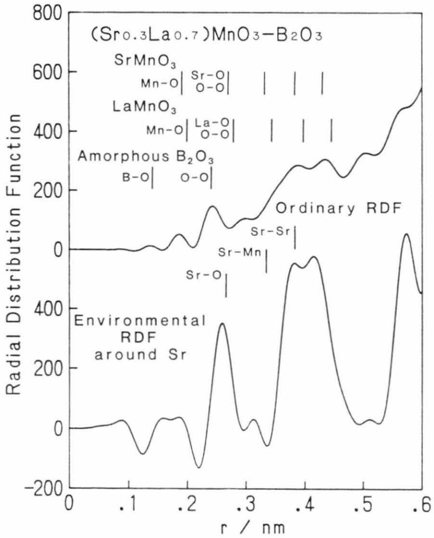

Fig. 2. Ordinary radial distribution function (RDF) (top) and environmental RDF around Sr (bottom) in vitreous $0.5\,La_{1-x}Sr_xMnO_3 0.5\,B_2O_3$

it is suggested that there exist in the sample structural features similar to the B_2O_3 glass. The Fourier transformation of $Q\,i(Q)$ gives the ordinary radial distribution function (RDF) at the top of Figure 2. The positions of some near-neighbor correlations of the perovskite $SrMnO_3$ [8] and $LaMnO_3$ [9], and atomic distances of B – O and O – O pairs in the B_2O_3 glass [6] are also shown in this figure. A small peak at 0.137 nm in the ordinary RDF indicates correlation between B and O. The coordination number of O around B computed from the area under the peak was estimated to be 3.0 ± 0.4. This value agrees well with the value 3.1 in B_2O_3 glass found by Warren et al. [6, 7], which is another evidence of the existence of B_2O_3 glass-like regions in the sample. Using Zachariasen's prediction [10], Warren et al. [6, 7] proposed a structural model of B_2O_3 glass where the fundamental local ordering units of BO_3 triangles are connected at their vertices to form a three dimensional random network. From the crystalline data, the second peak at 0.186 nm in the ordinary RDF is due to $Mn^{3+}-O$ and $Mn^{4+}-O$. Similarly, some pairs Sr – O, La – O and O – O may contribute to the third peak at 0.245 nm. The coordination number of oxygen around the manganese ions is estimated to be 5.7 ± 0.5. Taking account of the experimental error, the value agrees with the value 6 for the perovskite structure.

The AXS measurements were carried out with the synchrotron radiation source in the Photon Factory (PF) of the National Laboratory for High Energy Physics, Tsukuba, Japan. For details of the experimental setting and analysis cf. [11]. The scattering intensities observed at 15.106 and 16.081 keV below the Sr K-absorption edge (16.106 keV) are drawn with solid and dotted lines, respectively at the bottom of Fig. 3. The Sr $K\beta$ fluorescence was corrected for the scattering intensity at 16.081 keV [12]. The coherent intensities shown at the bottom of Fig. 3 were obtained by converting these measured intensities to electron units per atom. The profile is typical for an amorphous oxide except for the small shoulder at the low Q-side of the first peak, which, as has already been mentioned with Fig. 1, is the peak corresponding to the first peak of the B_2O_3 glass. The difference between these two intensities shown at the top of Fig. 3 is due to the change of the real part of the anomalous dispersion term of Sr [13]. The differential intensities at $Q < 16\ \mathrm{nm}^{-1}$ have been smoothly extrapolated to $Q = 0$. The effect of this extrapolation is known to give no critical contribution in the calculation of the radial distribution function (RDF) by the Fourier transformation [15, 16]. The oscillations in the differential intensity coincide with those in the original intensities, which is prominent in the first three broad peaks. It indicates that these oscillations are profoundly related to the Sr ions. Generally, oscillations which are still distinct in the high-Q region of an intensity profile result from the fact that species with definite bond lengths and angular relations are present [14]. The differential interference function $Q\,\Delta i(Q)$ calculated from the difference is shown with a dotted line in Figure 1.

The Fourier transform of $Q\,\Delta I(Q)$ gives the environmental RDF around Sr at the bottom of Fig. 2, which represents the local atomic arrangement around Sr. Since the contents of Sr are only 3 at% in the sample, the difference obtained by the anomalous dispersion effect of Sr is estimated to be less than a few percent of the observed intensity in a high-Q region. Since the error due to counting statistics is about 2% before taking the difference, the error in the differential profile raises by about 50% in the high-Q region. Thus, there are small oscillations in the differential profile which may cause the large oscillations on the lower-r side of the first peak in the environmental RDF. Nevertheless, the present authors maintain the view that essential structural features can be seen from these RDF data. The first peak at 0.259 nm in the environmental RDF around Sr is estimated to be due to $Sr-O$ pairs from the crystalline data. The coordination number of O around Sr computed from the area under the peak is 13.5 ± 1.4, which is to be compared with that in perovskite $SrMnO_3$, i.e. 12 at 0.269 nm.

Consequently, the present results suggest that the modulated regions observed in the transmission electron microscope [1] indicate to harmony between non-crystalline regions consisting of the random network structure of the BO_3 triangles and highly ordered perovskite-like regions. The ferromagnetic properties of this oxide glass may be ascribed to the latter regions. The magnetizations of the amorphous and crystalline states are known to be similar [17], and thus the present result supports the conclusion by Inomata et al. [1] that the ferromagnetism of the amorphous oxide is due to double-exchange interactions of $Mn^{3+}-O^{2-}-Mn^{4+}$ ions.

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