3A, 6C/2005G128

Analysis of Crystal Structure and Phase Transition of $Ba_{2-x}La_xIn_2O_{5+\delta}$ by Synchrotron X-Ray Diffraction at High Temperatures

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It was reported that crystal structure of $Ba_2In_2O_5$ changes from brownmillerite with ordered oxide ion vacancy to perovskite with random distribution of those at 910°C. Drastic increase of oxide ion conductivity due to the first order phase transition has also been reported. We have discovered second order phase transition at 1060°C in $Ba_2In_2O_5$ and concluded that the phase above 1060°C with the lowest activation energy for transport should be the most promising oxide ion conductor if the phase could be maintained at lower temperatures [1]. Since distortion from perovskite structure of this phase is the smallest, we have considered that one of the possible methods to stabilize high temperature phase of $Ba_2In_2O_5$ system is increase of oxide ion content by partial substitution of La^{3+} for Ba^{2+} site. In this study, crystal structure and phase transition behavior of $Ba_{2-x}La_xIn_2O_{5+\delta}$ have been studied. For precise analysis of crystal structure, synchrotron X-ray diffraction measurements at high temperatures have been carried out using originally designed furnace equipped at BL-3A or 6C in PF [2, 3].

The crystal structure of $Ba_2In_2O_5$ at room temperature was brownmillerite. Higher crystal symmetry was observed with increase of La content, resulting in cubic symmetry for $Ba_{1-x}La_xIn_2O_{5+\delta}$ with $0.5 \le x \le 1.0$. This suggests that decrease of concentration of oxide ion vacancy is effective to make the crystal symmetry at room temperature higher.

Fig. 1 shows the synchrotron X-ray diffraction patterns of $Ba_{2-x}La_xIn_2O_{5+\delta}$ at 1200°C. It was concluded that the crystal structure of $Ba_2In_2O_5$ at 1200°C was distorted perovskite since minor peaks, which could not be indexed as cubic, were observed. Crystal symmetry of $Ba_{1.8}La_{0.2}In_2O_{5.1}$ at 1200°C was higher than that of $Ba_2In_2O_5$ since number of the minor peaks decreased. X-ray diffraction pattern of $Ba_{1.3}La_{0.7}In_2O_{5.35}$ could be indexed as cubic perovskite, suggesting that decrease of oxide ion vacancy by La substitution is effective to make the crystal symmetry higher also at high temperatures.

The electrical conductivity of $Ba_{1.3}La_{0.7}In_2O_{5.5}$ showed similar behaviour to that of $Ba_2In_2O_5$ above 910°C. No drastic decrease of electrical conductivity with decrease of temperature below 910°C was observed in $Ba_{1.3}La_{0.7}In_2O_{5.5}$, showing agreement with the results of X-ray diffraction measurements.

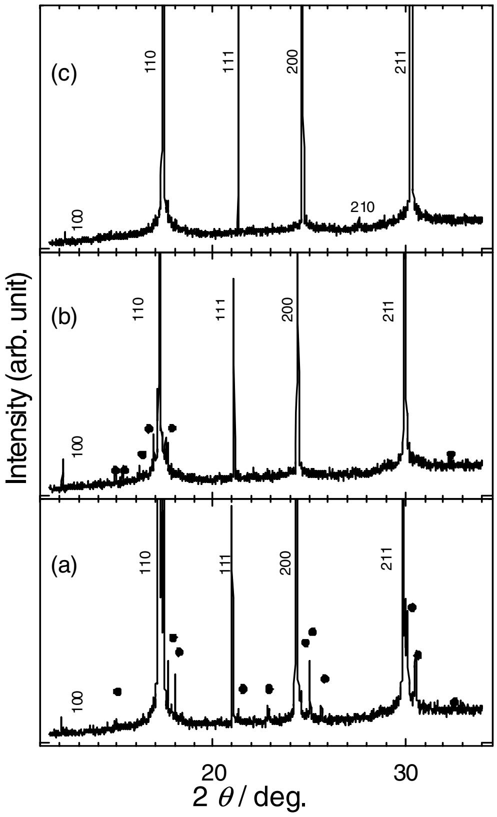

Fig.1 Diffraction patterns of $Ba_{2-x}La_xIn_2O_{5+\delta}$ at 1200°C obtained using X-ray with wavelength of 90.06pm from synchrotron radiation. (a) $Ba_2In_2O_5$, (b) $Ba_{1.8}La_{0.2}In_2O_{5.1}$ and (c) $Ba_{1.3}La_{0.7}In_2O_{5.35}$. Peaks represented by closed circle could not be indexed as cubic symmetry.

References

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