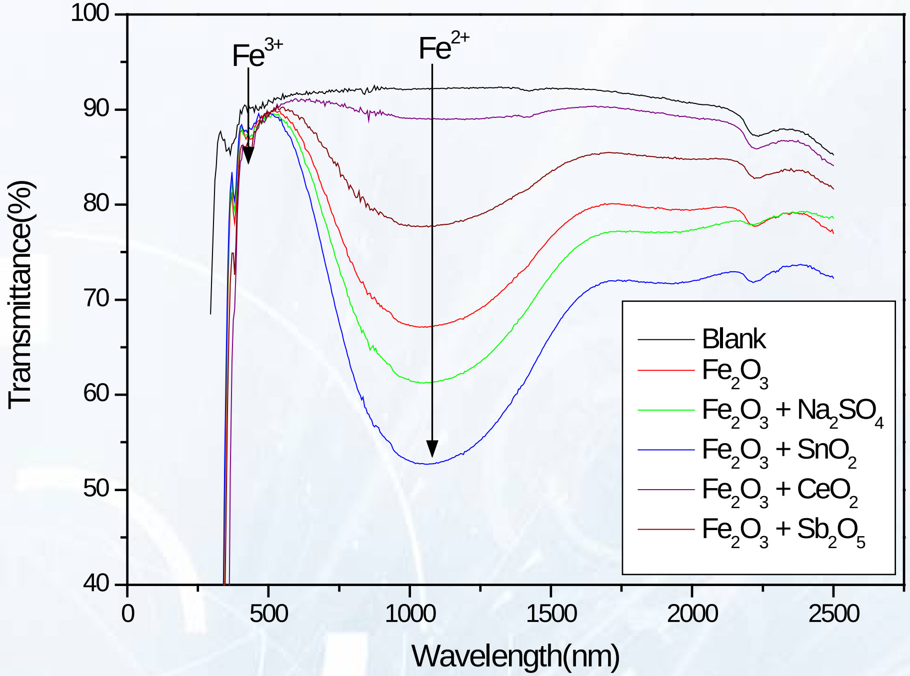
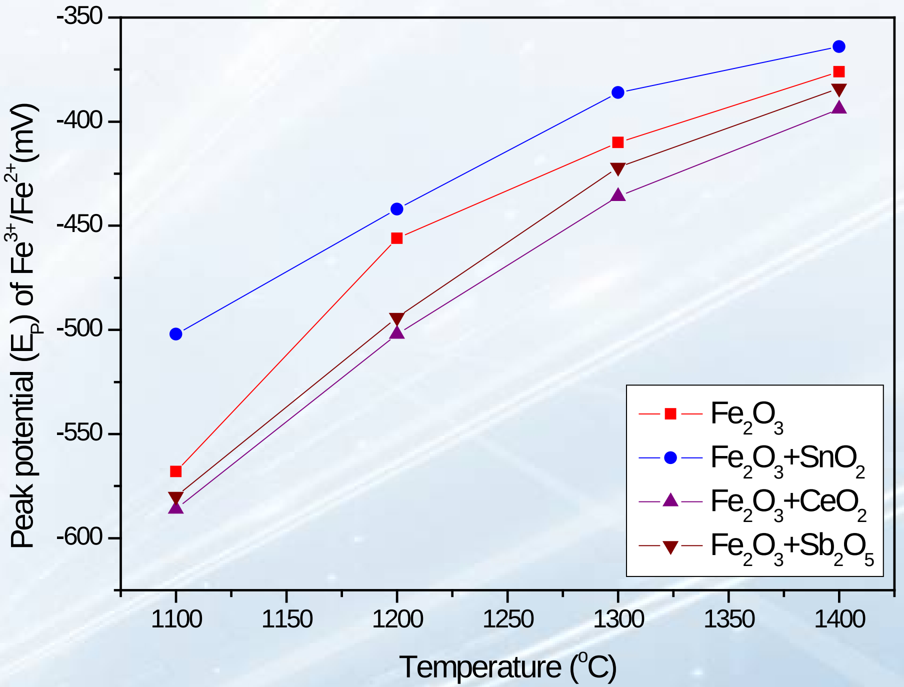
Spectroscopy and Voltammetry



Spectral transmission of all model glasses.



Temperature dependence of peak potential (E_p) due to Fe^{3+}/Fe^{2+} .

- ► **Spectroscopy at T_{1050nm}: Fe-redox; Fe+Sn>Fe+S>Fe>Fe+Sb>Fe+Ce**
- ► **Voltammogram at E_p: Fe-redox; Fe+Sn>Fe>Fe+Sb>Fe+Ce**

Redox Interaction derived from Glass State

Suggested Redox Interaction Reaction by Spectroscopy and Wet Chemical Analysis;

$$2Fe^{2+} + 2Ce^{4+} \rightleftarrows 2Fe^{3+} + 2Ce^{3+} \quad (1)$$

$$2Fe^{2+} + Sb^{5+} \rightleftarrows 2Fe^{3+} + Sb^{3+} \quad (2)$$

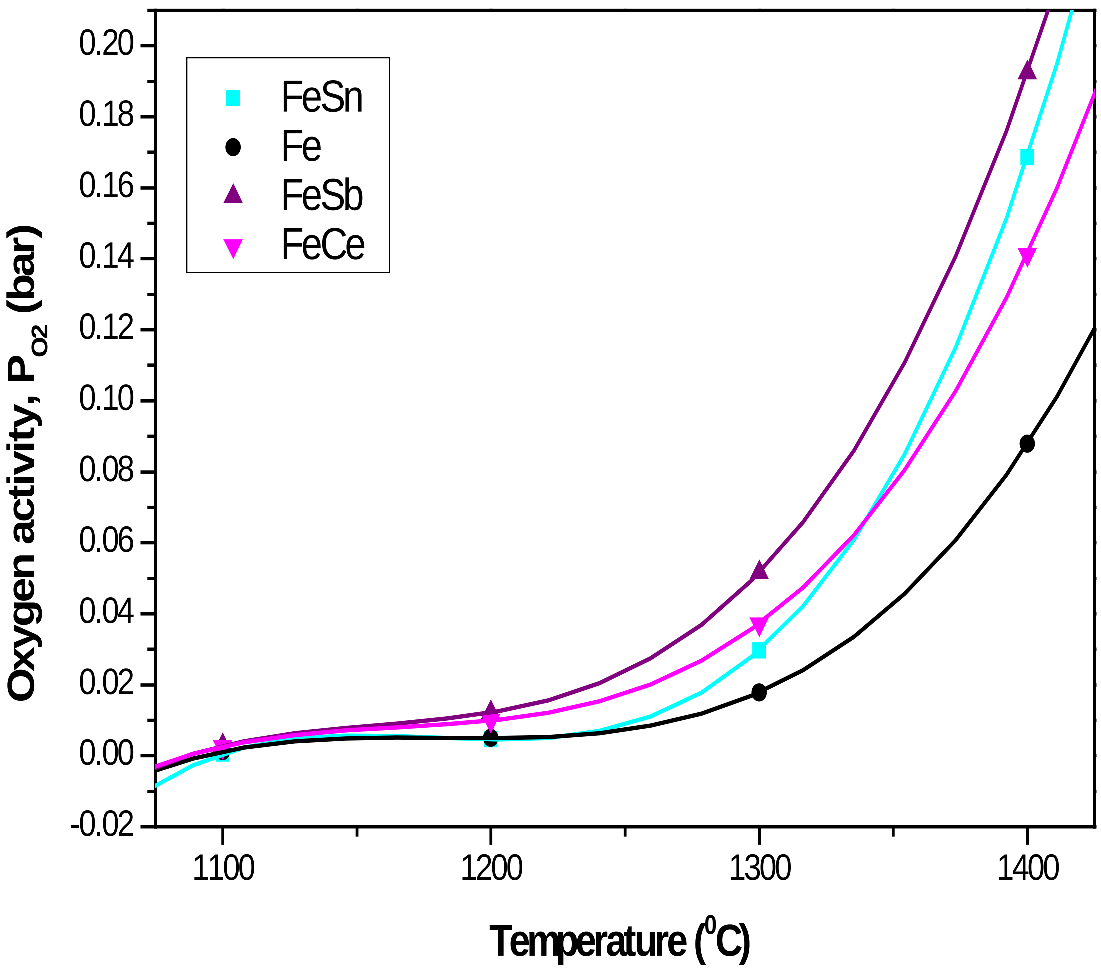
$$2Fe^{3+} + S^{4+} \rightleftarrows 2Fe^{2+} + S^{6+} \quad (3)$$

$$2Fe^{3+} + Sn^{2+} \rightleftarrows 2Fe^{2+} + Sn^{4+} \quad (4)$$

1) Is the redox interaction between Fe and M at room temperature valid also in the melt state?

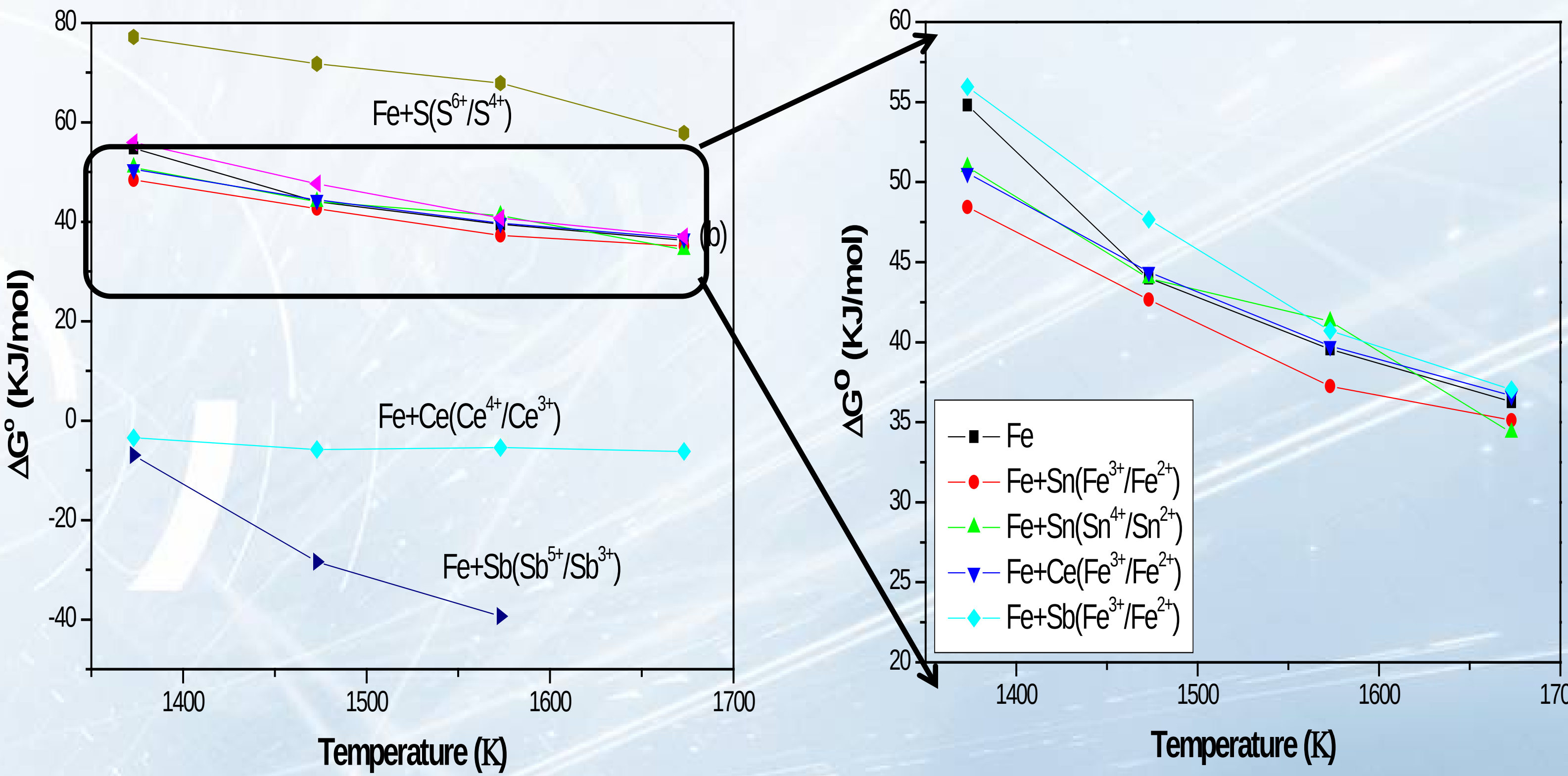
2) Why does the direction of Fe reduction reaction differ according to the secondary M partner?

Oxygen activity



Derivation of $\triangle G^0_{M^{(x+n)+}/M^{x+}}$ from E_P

$$E_P = \frac{T \cdot \Delta S^0}{n \cdot F} + \frac{-\Delta H^0}{n \cdot F} \Rightarrow \Delta H^0 - T\Delta S^0 = -n \cdot F \cdot E_P = \Delta \boldsymbol{G^0}_{M^{(x+n)+}/M^{x+}}$$



Redox Interaction Reaction based on $\triangle G^0_{M^{(x+n)+}/M^{x+}}$

Fe+Ce:	$2Fe^{2+} + 2Ce^{4+} \rightleftarrows 2Fe^{3+} + 2Ce^{3+}$	$\Delta G^0_{Fe^{3+}/Fe^{2+}} > \Delta G^0_{Ce^{4+}/Ce^{3+}}$
Fe+Sb:	$2Fe^{2+} + Sb^{5+} \rightleftarrows 2Fe^{3+} + Sb^{3+}$	$\Delta G^0_{Fe^{3+}/Fe^{2+}} > \Delta G^0_{Sb^{5+}/Sb^{3+}}$
Fe+S:	$2Fe^{3+} + S^{4+} \rightleftarrows 2Fe^{2+} + S^{6+}$	$\Delta G^0_{Fe^{3+}/Fe^{2+}} < \Delta G^0_{S^{6+}/S^{4+}}$?
Fe+Sn:	$2Fe^{3+} + Sn^{2+} \rightleftarrows 2Fe^{2+} + Sn^{4+}$	$\Delta G^0_{Fe^{3+}/Fe^{2+}} < \Delta G^0_{Sn^{4+}/Sn^{2+}}$

►**Equilibrium state of redox interaction reaction is explained rationally by $\triangle G^0_{M^{(x+n)+}/M^{x+}}$.**