The crystal structures of two Y_2O_3 and B_2O_3 containing pyroxenes

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The crystal structure of two Y_2O_3 and B_2O_3 containing pyroxenes occurring in glass ceramics used as solders in solid oxide fuel cells (SOFC) are described.

Y_2O_3, CaO, MgO and ZrO_2 containing aluminoborosilicate glass powders were sintered at a temperature of 850°C for 100h and 1000h. XRD, 3D ED and TEM-EDX measurements were done to investigate the evolution of the crystalline phase assemblage.

In the glass ceramic heat treated for 100h two different kinds of Y_2O_3 containing silicates could be identified via EDX. The first phase with the approximate composition $Y_{0.9}Ca_{0.1}MgSi_{1.1}B_{0.9}O_6$ exhibits a triclinic unit cell, crystallizes in space group $C\bar{1}$ and has a pyroxene like structure but with one SiO_4 group replaced by a BO_3 group (Figure 1a). As a result, the tetrahedral chain is broken up, since one of the bridging oxygens loses connection. This leads to a structural distortion which reduces the symmetry to triclinic. The Ca on the M2 position is almost completely replaced by Y to charge balance the substitution of Si by B.

The second phase with an approximate chemical composition of $Y_{0.5}Ca_{0.5}MgSi_{1.5}B_{0.5}O_6$ contains higher amounts of Ca and is a clinopyroxene with space group $C2/c$ with a structure similar to that of diopside. The M2 position shows much higher atomic displacement parameters compared to the other atoms in the structure and is occupied by both Ca and Y. On one face of the SiO_4 tetrahedra a residual potential could be observed in the difference Fourier map, which was interpreted as the presence of BO_3 triangles which partially replace the SiO_4 tetrahedra coupled with the replacement of Ca by Y on the M2 position. This could be confirmed by a split refinement of the chain position. The phase was interpreted as a disordered polysome of diopside and the previously described triclinic phase.

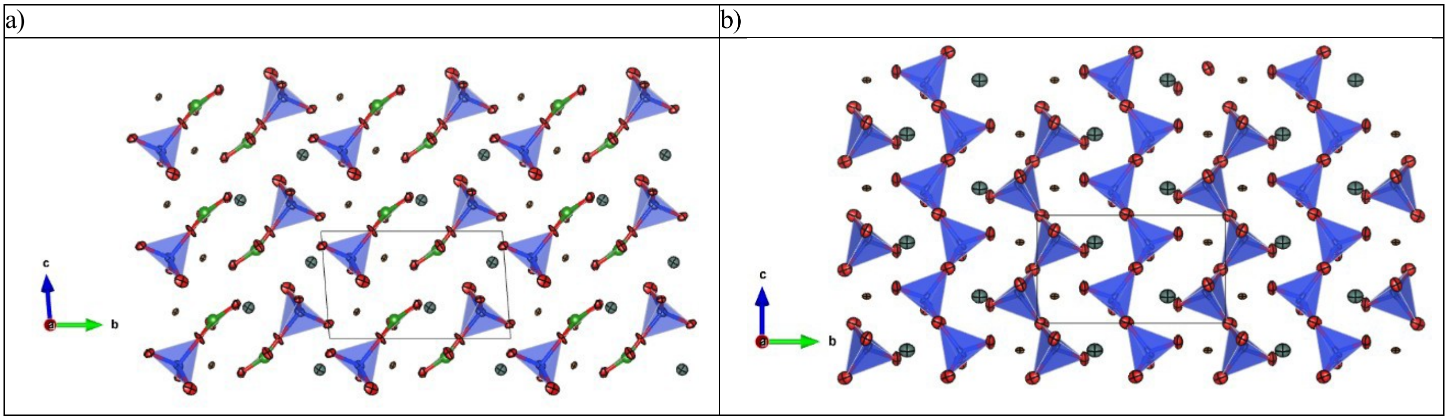

Figure 1. Crystal structure of a) the triclinic phase and b) the monoclinic phase viewed along the a-Axis. SiO_4 tetrahedra are blue, BO_3 groups are green, Mg and Y Atoms are orange and grey respectively. (Picture created using Vesta [1]).

After heat treatment for 1000h the disordered polysome contains no more Y and B and its unit cell parameters are now similar to those of pure diopside. The triclinic phase is not present anymore after 1000h and instead borates like $Mg_2B_2O_5$ or YBO_3 start to appear.

The herein presented results have implications for the stability of Y_2O_3 containing crystallizing glass solders in SOFCs. In addition, they show that B containing pyroxene like phases can be formed. In the case when the BO_3 groups are ordered on one position of the pyroxene chain, the symmetry is lowered to triclinic.

[1] Momma, K., Izumi, F. (2011). *J Appl Crystallogr* **44**, 1272.