Phase formation pathways of Me2+ oxides on sapphire (α-Al2O3) substrates

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Background

Aluminate structures present phase formation anomalies irrespective of the initial stoichiometry of the oxide powder mixes. In metal oxide systems (Me2+ or Me3+), multiphases form at different cation to aluminum (Mex+/Al) ratios. Singh and his colleagues observed multiple phase formation in starting mixture ratios of CaO to Al2O3; 1:1, 1:2 and 3:1. Even if the stoichiometry started from calcium or aluminum rich compositions, CA was present in the diffractograms (Singh et al. 1990. p.873). Previous studies on calcium aluminates suggested that large cation size of Ca2+ may create a difficulty of diffusion into the Al2O3 (Tian et al. 2016. p.104). Tian and his coworkers demonstrated the distribution of Ca-rich phases with backscattered electron (BSE) images towards the outer layers of the core shell structure. In the center of this core shell structure Al2O3/CA6 was present. We observed that the first forming phase in strontium, calcium and yttrium aluminate systems is 1:1 oxide compound SA (SrAl2O4), CA (CaAl2O4), and YAP (YAlO3) irrespective of the starting Mex+/Al3+. This study claims that the Mex+/Al ratio at the interface determines the first forming incipient phase. Also, it appeared that having a single type of Al-O coordination polyhedra is facilitating the phase formation in aluminate systems.

Methods

SrO-Al2O3 binary system have 6 compounds: Sr4Al2O7, Sr3Al2O6, SrAl2O4, Sr4Al14O25, SrAl4O7, and SrAl12O19 (Fig.1). Phase pure aluminate powders were synthesized using Pechini method. Crystallization temperatures of aluminate powders were determined with thermogravimetric analysis. Phase distribution above 800-900 °C, the first crystallization, was recorded with ex-situ XRD by 50-100 °C temperature slots. Isothermal heating of 1 hour was applied to compounds. The temperature was increased until there was no change in the phase distribution of each compound. These powders were used to acquire Al-L2,3 and O-K ELNES edges of phase pure aluminate compounds with different stoichiometry to be used as a fingerprint of the compound.

Heating temperatures of deposited substrates were selected for each compound in a way that samples were XRD phase pure of desired stoichiometry. Amorphous or crystalline precursors having different Ca/Al ratio were deposited on sapphire substrates with different orientations. The effect of changing stoichiometry at the interface of the reaction couple was adjusted as a coating. Each deposited substrate was characterized with scanning electron microscopy (SEM) and X-Ray diffractometry (XRD) before the sample preparation for transmission electron microscopy (TEM). Then, the first structure to form at the interface was analyzed with the help of high-resolution TEM (HRTEM), HR-STEM, and EELS-ELNES. Different aluminate compounds at the interphase between reaction couples were compared with ELNES fingerprint of each pure aluminate compound.

Results
All sapphire substrates were analyzed with X-ray diffractometry (XRD). Four strontium aluminates were identified with ELNES edges (Fig.2 a-d). Al-L2,3 edge at an energy of 73.1 eV was chosen as the fingerprint for each aluminate compound. K edge of oxygen is at 532.0 eV. We tried to identify the incipient structures at the interface of sapphire-aluminate film with different Sr2+/Al3+ ratio with the Al-L and O-K fingerprints of phase pure compounds.

Conclusion
Our study was a first attempt to clarify what kinetic constraints are determining the incipient metastable aluminate phase in Sr-, Ca-, Y- aluminate systems.

Graphic
Figure 1: Equilibrium binary phase diagram of SrO-Al2O3 (Van der Heggen, D. et al. 2022. p.3).

Figure 2. Al L2,3 ELNES edges of a) Sr4Al14O25 (S4A7), b) SrAl12O19 (SA6), c) SrAl4O7 (SA2) and d) Sr3Al2O6 (S3A), respectively.

Graphic:

Figure 1.

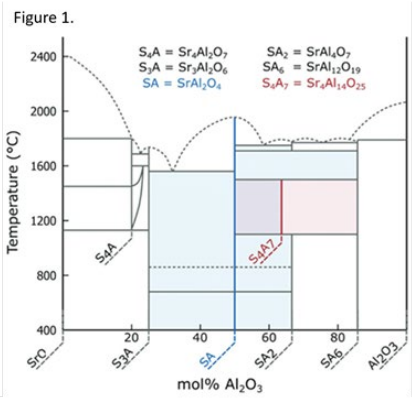
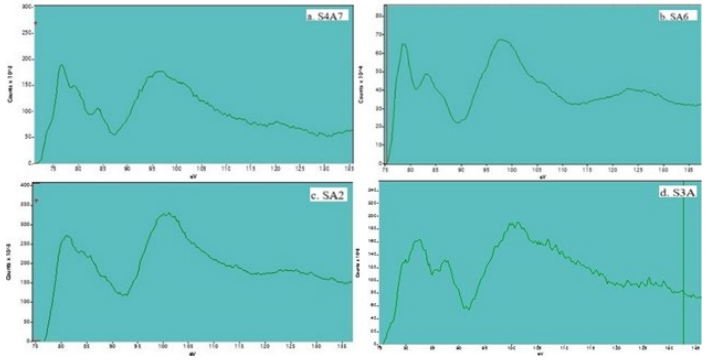


Figure 2.



Keywords:

Interface reactions, aluminates, interphase, EELS

Reference:

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