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Excess Oxygen in $12CaO\bullet 7Al_2O_3$ Studied by Thermogravimetric Analysis

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Oxygen radial (O_2^-, O^-)-accommodated $12CaO\bullet 7Al_2O_3$ (C12A7) releases oxygen molecules at about 800 °C when heated in helium. The corresponding weight loss nearly accords with that calculated from an amount of the accommodated radicals, providing solid evidence that they are formed by an oxygen gas uptake from the atmosphere. Small difference between the observed and calculated losses suggests the presence of peroxide ion, O_2^{2-}, which is confirmed by the enhancement of $770\,cm^{-1}$ band in Raman spectra of the radical-accommodated samples.

Formation of abundant oxygen radicals (O_2^- and O^-) as high as $10^{21}\,cm^{-3}$ in $12CaO\bullet 7Al_2O_3$ (C12A7)[1] is ascribed to its ability to incorporate various anions.[2] The unit cell is composed of a positively charged framework built from 12 cages, $[Ca_{24}Al_{28}O_{64}]^{4+}$. In the stoichiometric composition, two extra-framework O^{2-} ions per unit cell occupy different cages to preserve the charge neutrality. As has been confirmed by electron paramagnetic spin resonance (EPR) measurements,[3] the oxygen radicals are formed inside cages as a substitute for the O^{2-} ion when annealed in an oxidizing atmosphere. We have proposed that the oxygen radicals are formed by an uptake of oxygen gas from the atmosphere.[4] Therefore, their incorporation should accompany an excess weight over the stoichiometric composition. The purpose of this study is to observe directly the excess weight by thermogravimetric experiment to validate the oxygen radical formation due to the O_2 uptake. In addition, we examine the presence of peroxide ion, O_2^{2-}, in C12A7, which has been suggested in the previous work.[5] Although O_2^{2-} ions are undetectable by the EPR, they contribute to the excess weight.

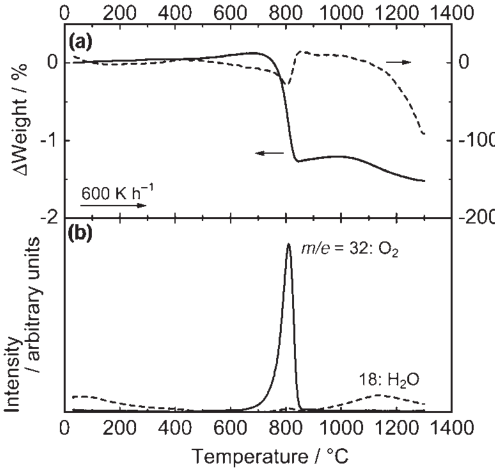

Figure 1. Thermogravimetric–evolved gas combined analyses of a C12A7 polycrystal annealed at 550 °C for 36 h in dry O_2. Results of thermogravimetric–differential thermal analyses (a) and mass spectroscopy (b) were recorded during heating with $600\,K\,h^{-1}$ and flowing He carrier gas.

Polycrystalline C12A7 sinters with a relative density of about 80% were heated at 1350 °C in dry oxygen atmosphere, and quenched to room temperature. Then, they were isothermally annealed at 550–725 °C for 2 to 128 h in the dry oxygen atmosphere to incorporate the oxygen radicals (O_2^-, O^-). Their concentrations were determined by EPR and Raman spectroscopy. The detail procedures how to determine their concentrations are described elsewhere.[4] The excess oxygen incorporated by the formation of the oxygen radicals is expressed as $3[O_2^-] + [O^-]$, where the brackets denote the molar fraction of relevant species. Samples used in this study contain the oxygen radicals with a concentration ranging from 2×10^{20} to $1 \times 10^{21}\,cm^{-3}$, which corresponds to the excess weight of 0.5–1.4%. One of sinters was annealed at 1000 °C for 2 h in wet helium to annihilate the excess oxygen species, especially O_2^- and O_2^{2-}, which possibly contribute to the Raman spectra. The annealed sinter was used as a reference sample for the Raman spectroscopy. 8 samples were subjected to thermogravimetric–evolved gas combined (TG–EG) analyses in dry helium atmosphere using a Rigaku thermoplus system.

Figure 1 shows an example of the TG–EG analyses. A considerably large weight loss was observed at about 800 °C with an endotherm. The intense Q-mass signal at $m/e = 32$, which is assigned to O_2, was observed corresponding to the weight loss. Maximum temperature in the weight loss rate coincided with that in the intensity of the O_2 signal in all samples. Moreover, the weight loss at about 800 °C has a good correlation with the integrated intensity of the O_2 signal. These facts clearly indicate that the weight loss is due to O_2 desorption. Another weight loss was observed at higher temperature range of about 1200 °C with endotherm, which is due to H_2O desorption. Such desorption is

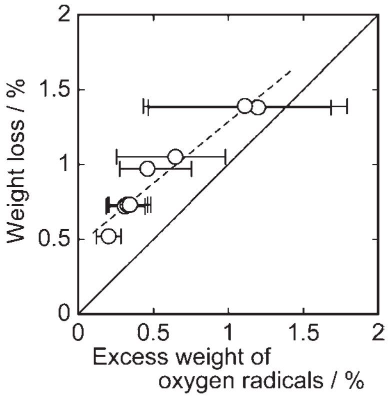

Figure 2. Relationship between excess weight derived form incorporation of oxygen radicals (O_2^- and O^-), and the weight loss at about 800 °C.

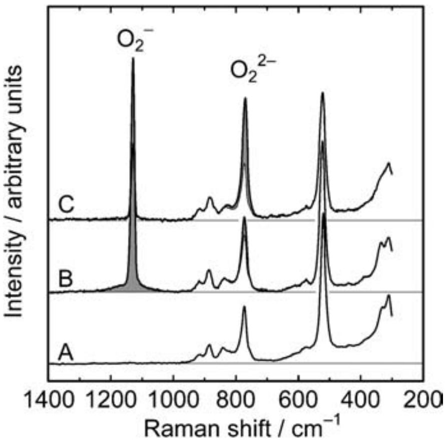

Figure 3. Raman spectra for C12A7 polycrystals annealed under conditions: (A) 1000 °C for 2 h in wet He (reference sample), (B) 550 °C for 32 h in dry O_2, and (C) 550 °C for 2 h in dry O_2. shadowed area corresponds to O_2^- and O_2^{2-}.

ascribed to H_2O impurities, which has been presumably adsorbed on and/or incorporated into the samples during the O_2 annealing or the TG–EG analyses.

According to the thermodynamic study in ref 4, the equilibrium total concentration of the oxygen radicals in helium (empirically, oxygen partial pressure of about 10^{-6} atm) at >800 °C is as low as 10^{17}–10^{18} cm^{-3}. Thus, the observed weight loss due to the O_2 desorption is caused by a shift of the equilibrium concentration with temperature and oxygen partial pressure. Since the initial concentration before the TG–EG test is 10^2–10^4 times higher than that after heating >800 °C, almost all (99–99.99%) of the initial oxygen radicals contribute to the weight loss.

Figure 2 plots relationship between the observed weight loss at about 800 °C and the excess weight estimated from the initial amount of the oxygen radicals, whose error principally comes from those in the EPR and Raman spectroscopy, and in the deconvolution process of the EPR spectra.[4] The weight loss nearly accords with the estimated loss, providing solid evidence that the oxygen radicals are formed by an uptake of oxygen from the atmosphere. However, the weight loss is always larger than the excess weight due to the oxygen radicals. This discrepancy (extra weight loss) suggests the presence of another kind of oxygen species that is formed in the oxygen-excess composition and is undetectable by the EPR or diamagnetic.

The most feasible candidate for the oxygen species is peroxide ion, O_2^{2-}, whose formation in C12A7 has been suggested from the Raman spectroscopy in the previous work.[5] Furthermore, its abundant formation has been reported in $Ca_{12}Al_{10}Si_4O_{35}$,[6] a Si-substituted derivative of C12A7. This has been clearly confirmed by Raman spectroscopy using $^{18}O_2$ isotope.[7] Figure 3 shows Raman spectra for the reference sample without O_2^-, O^-, nor O_2^{2-} (A) and oxygen-treated samples (B, C). Raman bands below 1000 cm^{-1} are mostly attributable to the vibrations in the lattice framework. Among them, Raman band at ca 770 cm^{-1} in C12A7 has been assigned to a stretching mode of AlO_4 tetrahedrons.[8] However, intensity of the 770 cm^{-1} band exhibits a considerable difference among the samples A, B, and C, indicating a superposition of another signal. Since the wave number, 770 cm^{-1} is well accords with a reported value for O_2^{2-} ion, and wavenumber shift from 1130 to 770 cm^{-1} is correlated to the bond order change in O_2^- and O_2^{2-},[9] the superposed signals indicated by shadowed areas in Figure 3 are assigned to the O_2^{2-} ion.

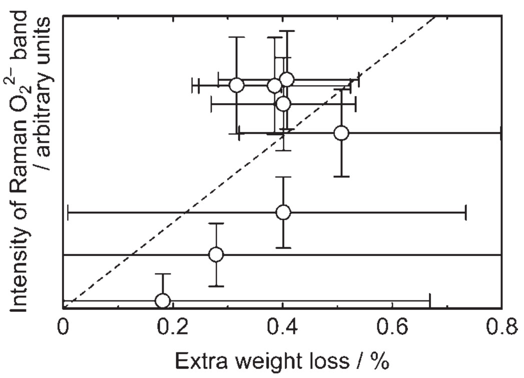

Figure 4. Relationship between the extra weight loss irrelevant to oxygen radicals (O_2^- and O^-) and intensity of Raman O_2^{2-} band at about 770 cm^{-1}.

In Figure 4, the intensity of shadowed area in the band at 770 cm^{-1} is plotted against the extra weight loss. Despite large error bars, two parameters correlate very well, further supporting the assignment of the 770-cm^{-1} band to O_2^{2-} ion and the formation of O_2^{2-} ions in C12A7. By using the relationship in Figure 4, the concentrations of O_2^{2-} ions in the samples are roughly estimated to be 5×10^{20} cm^{-3} at the maximum, which is comparable with the concentration of the oxygen radicals. The concentration of O_2^{2-} ions tends to decrease with an increase in the concentration of the oxygen radicals. This behavior suggests that the O_2^{2-} ions are formed at higher temperature and also contribute to the formation of oxygen radicals during an annealing at lower temperature by their conversion to the oxygen radicals.

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