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# Crystallographic Properties of $Ca_2Fe_2O_5$. Difference in Crystallographic Properties of Brownmillerite-like Compounds, $Ca_2Fe_2O_5$ and $Sr_2Fe_2O_5$, at Elevated Temperatures

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**Synopsis.** High-temperature X-ray diffraction analysis has revealed that $Ca_2Fe_2O_5$ remains in the original brownmillerite-like form up to *ca.* 1100 °C, whereas $Sr_2Fe_2O_5$ changes in crystal structure from brownmillerite to anion-deficient perovskite, without a change in oxygen content, above 700 °C.

It has been reported that $Sr_2Fe_2O_5$ has a cubic perovskite structure, without any change in the oxygen content, above 700 °C, whereas at room temperature this compound has an orthorhombic brownmillerite($Ca_2AlFeO_5$)-like structure.[1)] It has also been reported that the calcium analogue, $Ca_2Fe_2O_5$, is another brownmillerite-like compound at room temperature.[2)] The crystallographic affinity between both compounds at room temperature has assumed that $Ca_2Fe_2O_5$ also has a cubic perovskite structure with the oxygen vacancies statistically disordered at elevated temperature. In this paper the existence of an oxygen-deficient perovskite phase for $Ca_2Fe_2O_5$ at elevated temperature has been examined by means of high-temperature X-ray diffraction techniques. The results have been discussed in connection with the oxygen pressure effect on the preparation of $Fe^{4+}$-bearing perovskites, $CaFeO_3$ and $SrFeO_3$.

## Experimental

Dicalcium diiron(III) pentoxide $Ca_2Fe_2O_5$ was prepared by firing the appropriate mixture of $CaCO_3$ and $\alpha$-$Fe_2O_3$ in air at 1200 °C, with intermediate regrinding and refiring until a single phase product was obtained. Subsequently, the powder sample of composition $Ca_2Fe_2O_5$ was mounted on a platinum specimen holder in a high-temperature X-ray diffractometer. The X-ray measurement conditions and the calculation of the lattice parameters were the same as described in Ref. 1.

## Results and Discussion

The brownmillerite-like structure is referred to as an "ordered" oxygen-deficient perovskite structure.[3)] Therefore, there is a crystallographic relation between the orthorhombic brownmillerite-like structure and an ideal perovskite structure with cubic symmetry as follows : $a \simeq \sqrt{2}\,a_0$, $b \simeq 4a_0$, and $c \simeq \sqrt{2}\,a_0$, where $a$, $b$, and $c$ are the lattice constants of a brownmillerite-like phase and $a_0$ that for an ideal perovskite phase. On this basis new lattice parameters can be defined, $a'$, $b'$, and $c'$, for the dample $Ca_2Fe_2O_5$, where the three lattice constants have such a crystallographic relationship with the original orthorhombic cell constants, $a$, $b$, and $c$, as $a' = a/\sqrt{2}$, $b' = b/4$, and $c' = c/\sqrt{2}$.

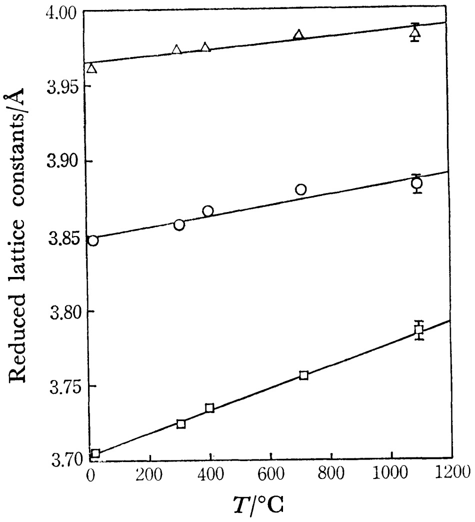

Fig. 1. Plots of reduced orthorhombic lattice constants *vs.* temperature for $Ca_2Fe_2O_5$.
△ : a′-axis, □ : b′-axis, ○ : c′-axis.

Figure 1 illustrates the reduced lattice constants of the sample of composition $Ca_2Fe_2O_5$ as a function of temperature. It may be seen that the three axes, $a'$, $b'$, and $c'$, expand linearly with increase in temperature in the range of temperature from 20 to 1093 °C, and that the three lines do not intersect. In other words, $Ca_2Fe_2O_5$ does not exist as a statistically disordered oxygen-deficient perovskite structure, but remains as a brownmillerite-like phase even at elevated temperatures. This result is quite different from that of $Sr_2Fe_2O_5$ obtained in a previous work.[1)]

For diiron(III) distrontium pentoxide, the $a'$-axis of the reduced cell begins to shrink at around 335 °C, and at 700 °C the three axes of the reduced orthorhombic cell meet, and consequently, the compound transforms to a cubic anion-deficient perovskite phase at temperatures above 700 °C (see Fig. 2, Ref. 1). From this it has been concluded that the oxygen atoms arranged regularly in the brownmillerite-like lattice begin abnormal thermal movement at around 335 °C. At 700 °C, a complete phase transition takes place as a result of the random displacement of the oxygen atoms or the vacancies throughout the oxygen lattice sites in the perovskite structure.

It is evident that the difference in movement of the oxygen ions at elevated temperatures between dicalcium and distrontium diiron(III) pentoxides is caused by differences in chemical composition between the double oxides, although the essential reason remains unclarified. The calcium ion has a smaller ionic radius than the Sr ion, so that the electrostatic binding energy must be higher in the Ca–O bonds than in the Sr–O bonds, as implied by the melting point of CaO. This assumption may be valid for the brownmillerite-like structure. In the brownmillerite-like structure, complete rows of oxygens are regularly missing from the ideal perovskite structure, and the accompanying movements of atoms result in tetrahedral coordination of the Fe atoms, and eight- or ninefold coordination about the alkaline-earth metal atoms, not twelvefold as in perovskite.³⁾ Consequently, the transition of $A_2Fe_2O_5$ (A=Ca or Sr) from brownmillerite-like structure to perovskite structure must be accompanied by a breaking of the A–O bonds and rearrangement of the component atoms. Therefore, it is reasonable to speculate that the binding energy of the Ca–O bonds in $Ca_2Fe_2O_5$ is so high that cleavage is difficult, so that $Ca_2Fe_2O_5$ is not transformed to an anion-deficient perovskite structure.

The experimental results and conclusions obtained in this work may explain why $CaFeO_3$ can only be synthesized under ultra high oxygen pressures[4] whereas $SrFeO_3$ can be readily prepared under less rigorous conditions,[5,6] *i.e.*, the energy necessary to break the Ca–O bonds in $Ca_2Fe_2O_5$ to yield $CaFeO_3$ by oxidizing the iron atoms from $Fe^{3+}$ up to $Fe^{4+}$ is higher than that which is necessary for $Sr_2Fe_2O_5$.

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