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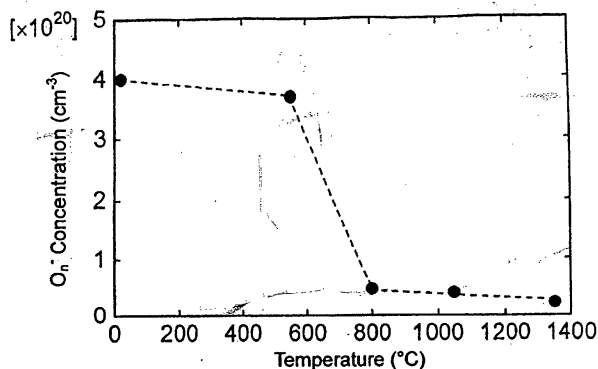
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(54) **12CaO 7Al<sub>2</sub>O<sub>3</sub> COMPOUND AND METHOD FOR PREPARATION THEREOF**

(57) There is provided a C12A7 compound capable of selectively and reversibly clathrating X<sup>-</sup> ions, such as active oxygen radicals, with improved controllability. The C12A7 compound clathrating OH<sup>-</sup> ions and On<sup>-</sup> at a concentration of 2 x 10<sup>19</sup> cm<sup>-3</sup> or less can be prepared by subjecting a mixed material containing Ca and Al to a solid phase reaction at a firing temperature not lower than 1200°C and lower than 1449°C in a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of 10<sup>-3</sup>

atm or less, keeping the resultant product at a temperature of 1200°C or higher, and cooling rapidly. The C12A7 compound is heat-treated to clathrate OH<sup>-</sup> ions at a concentration of 2 x 10<sup>19</sup> cm<sup>-3</sup> or less, and On<sup>-</sup> at a high concentration of more than 2 x 10<sup>19</sup> cm<sup>-3</sup>. The compound can reversibly clathrate or release On<sup>-</sup> ion radicals through the elevation or lowering of the temperature thereof in a temperature range of 300 to 850°C. The compound is useful for an oxidation catalyst, an anti-bacterial agent, an ion conducting material, an electrode for a solid-electrolyte fuel cell, and the like.

**Fig. 8**



## Description

## Technical Field

5 **[0001]** The present invention relates to a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound (referred to as C12A7) including a controlled amount of clathrated oxygen radicals and  $\text{OH}^-$  ions, a method for the preparation thereof, and an application thereof. More particularly, the present invention relates to C12A7 including monovalent anions represented by  $\text{X}^-$  and anion molecules at a low concentration, a method for the preparation thereof, a method of selectively and reversibly adding and releasing  $\text{On}^-$  ions to/from the compound with controllability, and an application of the C12A7 compound including  
10 a large amount of  $\text{On}^-$ . The  $\text{On}^-$  herein refers to  $\text{O}^-$  and  $\text{O}_2^-$ , where n is an integer of 1 or 2.

## Background Art

15 **[0002]** In 1970, H. B. Bartl et al., stated that in a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  crystal, two oxygen atoms of 66 oxygen atoms in a unit cell having two molecules do not belong to the network, but exist as "free oxygen" in a cage in the crystal (H. B. Bartl and T. Scheller, Neuses Jahrb. Mineral., Monatsh. 1970, 547).

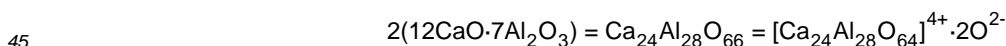
**[0003]** Hosono et al., of the present inventors discovered that  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  crystal clathrates  $\text{O}_2^-$  at a concentration of about  $1 \times 10^{19} \text{ cm}^{-3}$  as measured by electron spin resonance. The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  crystal was synthesized by subjecting a mixed material containing  $\text{CaCO}_3$  and  $\text{Al}_2\text{O}_3$  or  $\text{Al}(\text{OH})_3$  to a solid phase reaction at a temperature of  $1200^\circ\text{C}$   
20 in air. Hosono et al., proposed a model in which part of the free oxygen exists in the cage in the form of  $\text{O}_2^-$  (H. Hosono and Y. Abe, Inorg. Chem. 26, 1193, 1987, "Materials Science", Vol. 33, No. 4, pp. 171-172, 1996).

**[0004]** The present inventors subjected a mixed material containing calcium and aluminum at an atomic equivalent ratio of about 12:14 to a solid phase reaction under a controlled atmosphere and temperature, whereby a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound clathrating active oxygen at a high concentration of  $10^{20} \text{ cm}^{-3}$  or more was found. The present inventors  
25 filed patent applications of the compound itself, a method for production thereof, a measure for taking clathrated ions, a method of identification of active oxygen ion radicals, and an application of the compound (Japanese Patent Application Publication No. 2001-49524 = Japanese Unexamined Patent Application Publication No. 2002-003218, PCT/JP01/03252 = WO 01/79115 A1).

**[0005]** The present inventors synthesized a C12A7 compound containing  $\text{OH}^-$  at a concentration of  $10^{21} \text{ cm}^{-3}$  or more by hydrating the powder of the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound in water, a water-containing solvent, or a water vapor-containing gas and firing it under an oxygen atmosphere, and filed patent applications of the compound itself, a method  
30 for production thereof, a method of identification of  $\text{OH}^-$  ions, and an application of the compound (Japanese Patent Application Publication No. 2001-117546).

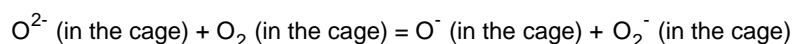
**[0006]** As to the mechanism by which the C12A7 compound includes the active oxygen radical ions at a high concentration, the present inventors consider that the free oxygen in the C12A7 compound is reacted reversibly with the oxygen molecules entering the C12A7 compound. As to the mechanism by which the  $\text{OH}^-$  ions are included at a high concentration, the present inventors consider that the free oxygen in the C12A7 compound is reacted reversibly with the water molecules entering the C12A7 compound. These mechanisms are described below in detail.  
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**[0007]** Fig. 1 is a schematic view showing the crystal structure of  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ .  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  is a cubic crystal system (lattice constant = 11.97 angstrom) belonging to a space group of  $I43d$ , including two formula of C12A7 per unit cell, and having a melting point of  $1449^\circ\text{C}$ . The crystal has a structure in which  $\text{Ca}^{2+}$  ions are coordinate with a network structure where tetrahedrons of  $\text{AlO}_4$  are aggregated. There is a cavity, i.e., a cage, in the crystal lattice.  
40



$\text{O}^{2-}$  is called free oxygen, and exists in the cage. In general,  $\text{O}^{2-}$  is always coordinated in the form of a cation in a solid structure, and does not exist in the free state. However, the  $\text{O}^{2-}$  ions in the cage of the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  crystal cannot be combined with the cations, and exist in the free state. This state is similar to the case that the ions are adsorbed  
50 on a solid surface, and is considered to be very chemically active.

**[0008]** The  $\text{O}^{2-}$  ions clathrated in the cage are prevented from directly reacting with the external atmosphere. However, when the temperature increases, the case size becomes large due to thermal expansion. Oxygen molecules in the atmosphere can pass through a bottle neck of the cage, to be thus clathrated in the cage. As a result, the reaction proceeds as follows:  
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**[0009]** Through this reaction, the C12A7 compound clathrates a large amount of active oxygen radical ions.

**[0010]** Two  $\text{O}_2^-$  are produced from two oxygen ions  $\text{O}^{2-}$  in the unit cell. The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound clathrating  $\text{O}_2^-$  at a high concentration is described as  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot(2-m)\text{O}_2^- (2m)\text{O}_2^-$ . In this formula,  $m \leq 2$ , and  $\text{O}_2^-$  and  $\text{O}^{2-}$  are clathrated in the cage. The oxygen molecules in the cage and in the atmosphere are equilibrated with the oxygen molecules in the atmosphere in a high temperature region in which the oxygen molecules can pass through the bottle neck of the cage. In general, when the temperature increases, the oxygen atoms in the C12A7 decrease in accordance with the Boyle-Charles law. Accordingly, it is considered that the number of active oxygen ion radicals decrease at a higher temperature.

**[0011]** When the synthesized C12A7 contains  $\text{H}_2\text{O}$ , the reaction of  $\text{O}^{2-}$  (in the cage) +  $\text{H}_2\text{O}$  (in the cage or in the interstices of the crystal lattice) =  $2\text{OH}^-$  (in the cage) proceeds, thus clathrating  $\text{OH}^-$  ions in the cage. The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound clathrating  $\text{OH}^-$  at a high concentration is described as  $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}\cdot(2-m)\text{O}^{2-}(2m)\text{OH}^-$ . In this formula,  $m \leq 2$ , and  $\text{OH}^-$  and  $\text{O}^{2-}$  are clathrated in the cage. The  $\text{H}_2\text{O}$  molecules in the cage are equilibrated with the water vapor in the atmosphere in a temperature region in which the  $\text{H}_2\text{O}$  molecules can pass through the bottle neck of the cage.

#### Disclosure of Invention

**[0012]** In an  $\text{X}^-$  ion clathration mechanism, a stoichiometric composition C12A7 is considered as a starting compound for clathrating  $\text{O}_2^-$  and/or  $\text{OH}^-$  at a high concentration. However, the existence of the compound and a method of producing the compound are not known. If a C12A7 compound including no  $\text{X}^-$  ions, i.e., a stoichiometric C12A7 compound containing oxygen ions, or a substantially stoichiometric C12A7 compound can be provided, it is expected that the  $\text{X}^-$  ions, such as the active oxygen radicals, are selectively and reversibly clathrated in the compound with improved controllability.

**[0013]** Since the  $\text{OH}^-$  ions are clathrated stably as compared with  $\text{O}_2^-$  ions and/or  $\text{O}^-$  ion radicals, the  $\text{OH}^-$  ions cannot be released into the atmosphere when they are fired at an elevated temperature of  $1200^\circ\text{C}$  or more for a prolonged time. The total concentration of the  $\text{X}^-$  ions is at most two times greater than that of the  $\text{O}^{2-}$ . Accordingly, the concentration of the  $\text{OH}^-$  ions clathrated in the C12A7 compound should be decreased in order to increase the concentration of other clathrated  $\text{X}^-$  ions such as  $\text{O}_2^-$  ion radicals. In other words, if the concentration of the  $\text{OH}^-$  ions included in the C12A7 compound can be decreased, the concentration of the clathrated  $\text{X}^-$  ions other than  $\text{OH}^-$  can be decreased.

**[0014]** The present inventors subjected a mixed material containing calcium and aluminum at an atomic ratio of about 12:14 to a solid phase reaction under controlled atmosphere and temperature to prepare a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound, kept the compound at a temperature of  $850^\circ\text{C}$  or more under a controlled atmosphere for a prolonged time, and then rapidly cooled the compound at a rate of about  $100^\circ\text{C}/\text{sec}$  or more, whereby C12A7 including  $\text{OH}^-$  ions and  $\text{O}_2^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less was prepared.

**[0015]** The compound is analogous to the stoichiometric C12A7 compound having 66 oxygen atoms (two oxygen ions clathrated in two cages and 64 oxygen atoms in the lattice) in a unit cell having two molecules. The compound is kept at a fixed temperature in the range of  $300$  to  $850^\circ\text{C}$ , preferably  $400$  to  $600^\circ\text{C}$ , or at slowly increasing or decreasing temperature under a controlled atmosphere, whereby the active oxygen radicals can be reversibly clathrated and released.

**[0016]** The mixed material containing calcium and aluminum at an atomic ratio of about 12:14, preferably mixed material containing calcium carbonate and  $\gamma$ -aluminum oxide at a molar ratio of 12:7, is subjected to a solid phase reaction as a high temperature not lower than  $1200^\circ\text{C}$ , and preferably not lower than  $1300^\circ\text{C}$ , under an atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3}$  atm or less, and preferably an oxygen partial pressure of 1 atm or more and a water vapor partial pressure of  $10^{-4}$  atm or less, whereby a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound is provided.

**[0017]** When the resultant compound is slowly cooled at a rate of about  $600^\circ\text{C}/\text{hr}$  or less, and preferably about  $100^\circ\text{C}/\text{hr}$  or less, under the atmosphere described above, the compound clathrates  $\text{O}_2^-$  ions at a concentration of more than  $10^{19} \text{ cm}^{-3}$  and the  $\text{OH}^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less.

**[0018]** The compound is kept at  $850^\circ\text{C}$  or more, and preferably  $900^\circ\text{C}$  or more, under the atmosphere described above, and is then rapidly cooled to  $300^\circ\text{C}$  or less, preferably room temperature, for example, at a rate of about  $100^\circ\text{C}/\text{sec}$  or more, whereby the  $\text{O}_2^-$  ions have a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less.

**[0019]** The C12A7 compound obtained in this way clathrates monovalent anions represented by  $\text{X}^-$  and anion molecules at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less. Examples of the monovalent anions represented by  $\text{X}^-$  and anion molecules include  $\text{OH}^-$ ,  $\text{O}_2^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{Au}^-$ . The clathrate amounts of the active oxygen  $\text{O}_2^-$  and/or  $\text{O}^-$  can be analyzed using an electron spin resonance or Raman scattering spectrum technique.

**[0020]** Figs. 2 and 3 show electron spin resonance spectra of the C12A7 compound clathrating  $\text{O}_2^-$  at room temperature and  $77\text{K}$ , respectively. The microwave frequency used was  $9.75 \text{ GHz}$ . At room temperature, an absorption band  $g = 2.02$  having a symmetric shape peaking at a magnetic field of  $343 \text{ mT}$  is observed. Using the absorption intensity,

the concentration of the clathrated  $\text{O}_2^-$  can be quantified. In the 77K absorption band, some structure is observed. The absorption band is provided by superposing an absorption band of the  $\text{O}_2^-$  ion radicals defined by  $g_x = 2.00$ ,  $g_y = 2.01$ , and  $g_z = 2.07$  on an absorption band of the  $\text{O}^-$  ion radicals defined by  $g_x = g_y = 2.04$ , and  $g_z = 2.00$ . Based on the intensity of each absorption band, the concentration of clathrated  $\text{O}_2^-$  and  $\text{O}^-$  ion radicals can be quantified.

**[0021]** Fig. 4 shows Raman scattering spectra of the C12A7 compound clathrating the  $\text{O}_2^-$  radical ions at a concentration of  $3 \times 10^{18} \text{ cm}^{-3}$  and  $3 \times 10^{20} \text{ cm}^{-3}$  at room temperature. The concentration of the  $\text{O}_2^-$  was quantified separately by electron spin resonance absorption band intensity. In the C12A7 compound including the  $\text{O}_2^-$  ion radicals at a concentration of  $3 \times 10^{20} \text{ cm}^{-3}$ , a Raman shift of  $1128 \text{ cm}^{-1}$  is due to  $\text{O}_2^-$  ion radicals. Using the Raman peak intensity, the amount of clathrated  $\text{O}_2^-$  can be quantified. The concentration of the clathrated  $\text{OH}^-$  ions can be analyzed using infrared absorption spectrum and Raman scattering spectrum techniques.

**[0022]** Fig. 5 shows infrared absorption spectra of the C12A7 compound clathrating  $\text{OH}^-$  at room temperature. Near  $3550 \text{ cm}^{-1}$ , an absorption band due to the  $\text{OH}^-$  is observed. From this absorption band, the concentration of the  $\text{OH}^-$  can be quantified using a molar extinction coefficient  $\epsilon$ . The molar extinction coefficient  $\epsilon$  is  $90 \text{ mol}^{-1} \text{ dm}^3 \text{ cm}^{-1}$ . Fig. 6 shows a Raman scattering spectrum of the C12A7 compound clathrating  $\text{OH}^-$  ions at room temperature. The peak of a Raman shift due to the  $\text{OH}^-$  ions is near  $3500 \text{ cm}^{-1}$ . Using the peak intensity, the concentration of the  $\text{OH}^-$  ions can be quantified. The concentration of the  $\text{OH}^-$  ions can be quantified using a nuclear magnetic resonance spectrum. On the other hand, the C12A7 will clathrate  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ , and  $\text{Au}^-$  only when they are intentionally added.

**[0023]** When the water vapor partial pressure upon firing is  $10^{-3}$  atm or more, the concentration of the clathrated  $\text{OH}^-$  ions exceeds  $2 \times 10^{19} \text{ cm}^{-3}$ . When the compound is fired at  $1200^\circ\text{C}$  or more under an atmosphere with an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3}$  atm or less, and preferably an oxygen partial pressure of 1 atm or more and a water vapor partial pressure of  $10^{-4}$  atm or less, the concentration of the  $\text{OH}^-$  ions can be decreased. In this case, the compound should be kept at this temperature for a prolonged time.

**[0024]** If the firing temperature is less than  $1200^\circ\text{C}$ , the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound is not well synthesized, even if the compound is fired under an atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3}$  atm or less. If the firing temperature exceeds  $1449^\circ\text{C}$ , the raw material melts, whereby the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound is not well synthesized. When the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound is synthesized by the solid phase reaction, calcium carbonate and  $\gamma$ -aluminum oxide are suitable for the raw material. Also, the compound can be synthesized using a combination of calcium hydroxide or calcium oxide with aluminum hydroxide or various aluminum oxides ( $\alpha$ ,  $\delta$ ,  $\theta$  phases).

**[0025]** The electron spin resonance spectrum of the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound including the active oxygen at 77K is provided by superposing a spectrum defined by  $g_x = 2.00$ ,  $g_y = 2.01$ , and  $g_z = 2.07$  on a spectrum defined by  $g_x = g_y = 2.04$ , and  $g_z = 2.00$ . Since these g values correspond to the g values of the  $\text{O}_2^-$  ion radicals and the  $\text{O}^-$  ion radicals in the solid, it is concluded that the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound clathrates the  $\text{O}_2^-$  ion radicals and the  $\text{O}^-$  ion radicals.

**[0026]** The ESR absorption band is symmetric at room temperature, and is asymmetric at a low temperature of 77K. This corresponds to the fact that the  $\text{O}_2^-$  ion radicals and the  $\text{O}^-$  ion radicals rotate in the cage at room temperature but are combined electrostatically with  $\text{Ca}^{2+}$  ions on the walls of the cage and fixed spatially. Using the absorption intensity, the concentration of the  $\text{O}_2^-$  ion radicals and the  $\text{O}^-$  ion radicals can be quantified.

**[0027]** The Raman scattering spectrum of the compound has a strong scattering peak near  $1130 \text{ cm}^{-1}$ . This peak corresponds to the Raman shift of the  $\text{O}_2^-$  ion radicals, which was reported by K. Nakamoto et al., (K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 1978, Wiley). The ESR absorption band correlates with the Raman scattering intensity. Using Raman scattering intensity, the intensity of the clathrated  $\text{O}_2^-$  ion radicals can be quantified.

**[0028]** The C12A7 compound including the  $\text{O}_2^-$  ion radicals at a high concentration of more than  $2 \times 10^{19} \text{ cm}^{-3}$  includes  $\text{OH}^-$  at a concentration of only  $2 \times 10^{19} \text{ cm}^{-3}$  or less. The concentration of the  $\text{OH}^-$  can be quantified using the infrared absorption spectrum near  $3560 \text{ cm}^{-1}$  (Japanese Patent Application No. 2001-117546).

**[0029]** The resultant C12A7 compound including the  $\text{OH}^-$  ions at a clathrate concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less and  $\text{O}_2^-$  ions at a clathrate concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less is kept at a fixed temperature in the range 300 to  $850^\circ\text{C}$ , and preferably 400 to  $600^\circ\text{C}$ , under a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more, and preferably 1 atm or more, and a water vapor partial pressure of  $10^{-3}$  atm or less, whereby the  $\text{O}_2^-$  ions can be included in the compound at a high concentration of more than  $2 \times 10^{19} \text{ cm}^{-3}$ .

**[0030]** Instead of maintaining the compound at the fixed temperature, the C12A7 compound fired at a high temperature under a dry oxygen atmosphere may be cooled. In a temperature range of 300 to  $850^\circ\text{C}$ , the compound may be slowly cooled. The slow cooling rate depends on the size of the crystal particles grown by firing the C12A7 compound, and may be approximately  $600^\circ\text{C/hr}$  or less.

**[0031]** The  $\text{O}_2^-$  ions contained in the C12A7 compound are equilibrated with the oxygen molecules in the atmosphere via the clathrated oxygen molecules. At a high temperature of  $300^\circ\text{C}$  or more, some of the  $\text{O}_2^-$  ions are exchanged with the oxygen molecules in the atmosphere. Once the C12A7 compound becomes electrically insulating, the compound takes electrons from the  $\text{O}_2^-$  ions in order to keep electrical neutrality. The  $\text{O}_2^-$  ions are released into the at-

mosphere as electrical neutral oxygen radicals ( $O \cdot$ ) or oxygen molecules. When an electric field is applied to the compound to externally supply electrons, the  $On^-$  ions can be released into the atmosphere as is.

**[0032]** When the compounds or the molecules that are easily oxidized are attached to the surfaces of the  $On^-$  ions, the  $On^-$  ions, especially the  $O^-$  ion radicals, oxidize the attached compounds or molecules. In this case, the electrons move from the oxidized compounds or molecules to the C12A7 compound, whereby the electrical neutrality can be kept. Since the  $O_2^-$  ion radicals and/or the  $O^-$  ion radicals disposed near the surface are easily moved and released, the compound that is easily oxidized, such as a hydrocarbon compound, is oxidized even at a temperature lower than 300°C.

**[0033]** In other words, since the oxidation occurs on the surface of the C12A7 compound at a temperature lower than 300°C, the C12A7 compound can be used as an oxidation catalyst or an antibacterial agent that can act at a temperature lower than 300°C.

**[0034]** The  $On^-$  ion radicals clathrated in the C12A7 are taken by the electric field. Alternatively, when the  $On^-$  are consumed by the reaction with the oxidized material,  $O_2$  in the atmosphere is taken into the C12A7 and is reacted with  $O_2^-$  to produce the  $On^-$  ion radicals.

**[0035]** Thus, when the C12A7 compound is kept at 300 to 850°C, the compound functions to convert the oxygen molecules in the atmosphere to  $O_2^-$  ion radicals and/or  $O^-$  ion radicals. Accordingly, when the compound is kept in the oxygen-containing atmosphere, an oxidation catalytic action can be continued. When exhaust gas containing oxygen emitted from an automobile engine is contacted with the C12A7 compound, incomplete combustion compounds such as hydrocarbons and carbon particles contained in the exhaust gas can be oxidized. Therefore, the C12A7 compound is effective as a catalyst for purifying the exhaust gas of automobile engines.

**[0036]** Since the  $On^-$  ions, oxygen ions or oxygen molecules can be released at a high temperature of 300°C or more, the  $12CaO \cdot 7Al_2O_3$  of the present invention can be used to oxidize organic materials. The  $On^-$  ions, especially  $O^-$  ions are known to have antibacterial properties. Therefore, the  $12CaO \cdot 7Al_2O_3$  clathrating a large quantity of the  $On^-$  ions of the present invention can be used as an antibacterial agent. The oxidation reaction on the surface may be performed at a temperature lower than 300°C.

**[0037]**  $On^-$ , kept within the compound at 850°C or less, exists relatively freely and can move within the crystal. Therefore, the  $12CaO \cdot 7Al_2O_3$  of the present invention can be used as an ion conductor. The C12A7 compound clathrating the  $X^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less, i.e., including the clathrated  $O^{2-}$  ions at a high concentration, can be used as an ion conductor utilizing the movement of the  $O^{2-}$  ions. When the ion conductivity and the ability to oxidize various compounds, both properties exhibited by the present compound, are combined, the present compound can be used as an electrode material for an oxide solid-electrolyte fuel cell.

#### Brief Description of the Drawings

#### **[0038]**

Fig. 1 is a schematic view showing the crystal structure of  $12CaO \cdot 7Al_2O_3$  (C12A7 compound).

Fig. 2 is a graph showing an example of an electron spin resonance spectrum of the C12A7 compound including  $On^-$  at room temperature.

Fig. 3 shows graphs of examples of electron spin resonance spectra of the C12A7 compound including only the  $O^-$  ( $3 \times 10^{18} \text{ cm}^{-3}$ ) ion radicals, and the C12A7 compound including both the  $O^-$  ( $2 \times 10^{20} \text{ cm}^{-3}$ ) and  $O_2^-$  ( $3 \times 10^{20} \text{ cm}^{-3}$ ) ion radicals at 77K.

Fig. 4 shows graphs of examples of Raman scattering spectra of the C12A7 compound including  $O_2^-$  ion radicals at a concentration of  $3 \times 10^{20} \text{ cm}^{-3}$ .

Fig. 5 shows graphs of examples of infrared absorption spectra of  $OH^-$  ions near  $3560 \text{ cm}^{-1}$ .

Fig. 6 shows a graph of an example of a Raman scattering peak of  $OH^-$  ions near  $3500 \text{ cm}^{-1}$ .

Fig. 7 shows graphs of mass changes by increasing or decreasing the temperature of the  $12CaO \cdot 7Al_2O_3$  compound in EXAMPLE 2.

Fig. 8 is a graph showing the  $On^-$  concentration of the rapidly cooled  $12CaO \cdot 7Al_2O_3$  compound in EXAMPLE 2.

Fig. 9 is a graph showing a change in the concentration of the  $OH^-$  ions clathrated in the  $12CaO \cdot 7Al_2O_3$  compound versus firing time at a temperature of 1300°C.

#### Best Mode for Carrying Out the Invention

**[0039]** Embodiments of the present invention will be described below.

## EXAMPLE 1

**[0040]** A mixed material containing calcium carbonate and  $\gamma$ -alumina at a molar ratio of 12:7 was fired at 1300°C for 2 hours under an atmosphere having a water vapor partial pressure of  $10^{-4}$  atm or less. Then, the mixed material was transferred to a room temperature region under a dry oxygen atmosphere of 1 atm, and was contacted with a water-cooled platinum block disposed therein. The cooling rate in the cooling step was about 100°C/sec. The resultant compound was confirmed to be a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound by X-ray diffraction.

**[0041]** The  $\text{OH}^-$  ion concentration contained in the resultant compound was quantified by infrared absorption spectroscopy and Raman scattering spectroscopy, and was found to be  $2 \times 10^{19} \text{ cm}^{-3}$  or less. The  $\text{O}_2^-$  ion radical concentration contained in the resultant compound was quantified by an electron spin resonance spectroscopy, and was found to be  $1.5 \times 10^{19} \text{ cm}^{-3}$ . Thus, it was demonstrated that by rapidly cooling the C12A7 compound to room temperature under the dry oxygen atmosphere, C12A7 including  $\text{OH}^-$  ions and  $\text{O}_2^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less was obtained.

## EXAMPLE 2

**[0042]** A mixed material containing calcium carbonate and  $\gamma$ -alumina at a molar ratio of 12:7 was fired at 1300°C for 2 hours under a dry oxygen atmosphere of 1 atm having a water vapor partial pressure of  $10^{-4}$  atm or less, and was slowly cooled at a rate of 600°C/hr under the dry oxygen atmosphere of 1 atm. The resultant compound was confirmed to be a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound by X-ray diffraction. The  $\text{OH}^-$  ion concentration contained in the resultant compound was quantified by infrared absorption spectroscopy and Raman scattering spectroscopy, and was found to be  $2 \times 10^{19} \text{ cm}^{-3}$  or less. The  $\text{O}_2^-$  ion concentration contained in the resultant compound was quantified by electron spin resonance spectra, and  $\text{O}_2^-$  ion radical and  $\text{O}_2^-$  ion radical concentrations were found to be  $3 \times 10^{20} \text{ cm}^{-3}$  and  $2 \times 10^{20} \text{ cm}^{-3}$ , respectively. Thus, by slowly cooling the C12A7 compound to room temperature under the dry oxygen atmosphere, C12A7 including  $\text{OH}^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less and  $\text{O}_2^-$  ions at a concentration of  $5 \times 10^{20} \text{ cm}^{-3}$  was obtained.

## EXAMPLE 3

**[0043]** A mixed material containing calcium carbonate and  $\gamma$ -alumina at a molar ratio of 12:7 was fired at 1300°C for 2 hours under water vapor-containing air (an oxygen partial pressure of 0.2 atm and a water vapor partial pressure of  $10^{-3}$  atm) was further fired at 1300°C for 2 hours under an atmosphere having a dry oxygen pressure of 1 atm, and was slowly cooled at a rate of 600°C/hr under the 1-atm dry oxygen atmosphere. The resultant compound was confirmed to be a  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound by X-ray diffraction.

**[0044]** The  $\text{OH}^-$  ion concentration contained in the resultant  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound was quantified by infrared absorption spectroscopy and Raman scattering spectroscopy, and was found to be  $2 \times 10^{19} \text{ cm}^{-3}$  or less. The  $\text{O}_2^-$  ion radical concentration clathrated in the compound was quantified by ESR and Raman scattering spectroscopy, and was found to be  $3 \times 10^{20} \text{ cm}^{-3}$ . The  $\text{O}^-$  ion radical clathrate concentration was verified by ESR spectroscopy, and was found to be  $2 \times 10^{20} \text{ cm}^{-3}$ .

**[0045]** The total amount of the  $\text{O}_2^-$  clathrated in the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound obtained in EXAMPLES 2 and 3 was  $5 \times 10^{20} \text{ cm}^{-3}$ , that is, 0.8 per unit cell, which was 20% of the theoretically estimated maximum total value  $2 + 2 = 4$ .

## EXAMPLE 4

**[0046]** The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound in EXAMPLE 2 was measured for mass changes by increasing or decreasing the temperature under vacuum. Fig. 7 shows the result. The compound obtained in EXAMPLE 1 had reduced mass in a temperature range of 600 to 1350°C with a temperature increasing curve. Corresponding to the temperature increasing curve, the compound had increased mass in temperature ranges of 1400 to 900°C and 800 to 600°C with a temperature decreasing curve.

**[0047]** The  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound in EXAMPLE 2 was slowly cooled at a rate of 4°C/min under a dry oxygen atmosphere to each temperature (1350°C, 1050°C, 800°C and 550°C) represented by circles in the decreasing temperature curve, was kept at each temperature for 30 minutes, and was then rapidly cooled to room temperature at a rate of about 100°C/sec. The  $\text{O}_2^-$  ion concentration contained in each rapidly cooled compound was quantified by electron spin resonance spectroscopy. Fig. 8 shows the resultant  $\text{O}_2^-$  ion concentration. The concentration represents the amount of the clathrated  $\text{O}_2^-$  ions at the temperature when the rapid cooling started.

**[0048]** It was found that clathration of the  $\text{O}_2^-$  ions started at about 550°C, the clathration amount thereof was gradually decreased at higher temperature, and the  $\text{O}_2^-$  ions were clathrated only at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less at 850°C or more. It was also found that the clathration was reversible and the  $\text{O}_2^-$  ions could be released to the

atmosphere by increasing or decreasing the temperature. Furthermore, it was demonstrated that by rapidly cooling the sample from a high temperature of 850°C or more, C12A17 including  $\text{On}^-$  ions and  $\text{OH}^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less was obtained.

## 5 COMPARATIVE EXAMPLE 1

[0049] Mixed powder of  $\text{CaCO}_3$  and  $\gamma\text{-Al}_2\text{O}_3$  with a molar ratio of 12:7 was subjected to a solid phase reaction at 1300°C under an atmosphere having a water vapor pressure of  $8 \times 10^{-3} \text{ atm}$ , and cooled to room temperature at a rate of 600°C/hr. The resultant powder was isostatic pressed at a pressure of 200 MPa to provide a green compact. The green compact was fired at 1300°C for 12 to 48 hours under a dry oxygen atmosphere having an oxygen partial pressure of 1 atm and a water vapor partial pressure of  $10^{-4} \text{ atm}$  or less. The  $\text{OH}^-$  ion concentration contained in each sample fired for 12, 24 or 48 hours was quantified by infrared absorption spectroscopy.

[0050] Fig. 9 shows the firing time dependence of the  $\text{OH}^-$  ion concentration. Fig. 9 reveals that the C12A7 compound synthesized under the atmosphere containing water vapor at  $1 \times 10^{-4} \text{ atm}$  or more includes  $\text{OH}^-$  ions at a concentration of  $1 \times 10^{20} \text{ cm}^{-3}$  or more, and that the compound continues to clathrate the  $\text{OH}^-$  ions at a concentration of  $1 \times 10^{19} \text{ cm}^{-3}$  or more when the compound is fired at 1300°C for 1000 hours under a dry oxygen atmosphere.

[0051] In other words, it was found that the compound included the  $\text{OH}^-$  ions at a high concentration of more than  $2 \times 10^{19} \text{ cm}^{-3}$  when the compound was fired at high water vapor pressure, and that, once the  $\text{OH}^-$  ions were clathrated, the concentration of the  $\text{OH}^-$  ions did not decrease in a short time even if the compound was fired under dry oxygen.

## 20 Industrial Applicability

[0052] The present invention provides a C12A7 compound capable of selectively and reversibly clathrating  $\text{X}^-$  ions, such as active oxygen radicals, with improved controllability.

[0053] The compound can reversibly clathrate or release  $\text{On}^-$  ion radicals through the elevation or lowering of the temperature thereof in a temperature range of 300 to 850°C. The compound is useful for an oxidation catalyst, an anti-bacterial agent, an ion conducting material, an electrode for a solid-electrolyte fuel cell, and the like.

## 30 Claims

1. A  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound clathrating monovalent anions represented by  $\text{X}^-$  and anion molecules at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less.

2. A  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, wherein the  $\text{X}^-$  are  $\text{OH}^-$  ions and  $\text{On}^-$  ion radicals, where n is an integer of 1 or 2.

3. A  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound clathrating  $\text{OH}^-$  ions at a concentration of  $2 \times 10^{19} \text{ cm}^{-3}$  or less, and  $\text{On}^-$  at a high concentration of more than  $2 \times 10^{19} \text{ cm}^{-3}$ .

4. A method for preparing the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1 or 2, comprising the steps of:

subjecting a mixed material containing calcium (Ca) and aluminum (Al) to a solid phase reaction at a firing temperature not lower than 1200°C and lower than 1449°C in a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3} \text{ atm}$  or less, keeping the resultant product at a temperature of 1200°C or higher, and cooling rapidly.

5. A method for preparing the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 3, comprising the steps of:

subjecting a mixed material containing calcium (Ca) and aluminum (Al) to a solid phase reaction at a firing temperature not lower than 1200°C and lower than 1449°C in a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3} \text{ atm}$  or less, and slowly cooling the resultant product to a temperature in the range of 300 to 850°C.

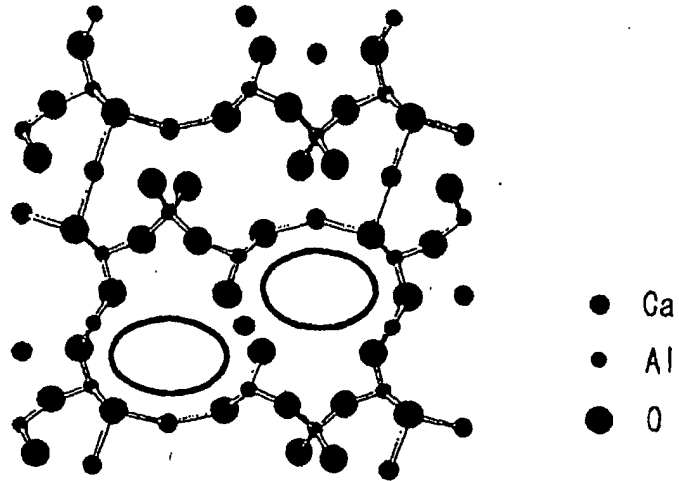
6. A method for preparing the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 3, wherein the  $12\text{CaO} \cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1 or 2 is kept at a fixed temperature in a temperature range of 300 to 850°C in a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3} \text{ atm}$

or less, and is cooled rapidly or slowly to room temperature.

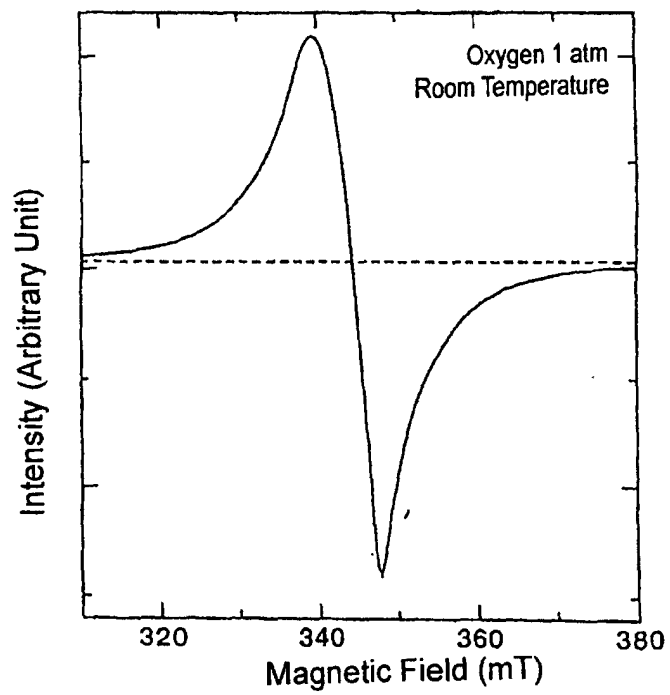
- 5
7. A method for reversibly clathrating or releasing  $\text{O}_n^-$  ion radicals through the elevation or lowering of the temperature of the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, 2 or 3 in a temperature range of 300 to 850°C in a dry oxygen atmosphere having an oxygen partial pressure of 0.1 atm or more and a water vapor partial pressure of  $10^{-3}$  atm or less.
- 10
8. A method for preparing the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 4 or 5, wherein calcium carbonate, calcium hydroxide, or calcium oxide is used as a raw material for the calcium, and aluminum oxide or aluminum hydroxide is used as a raw material for the aluminum.
- 15
9. An oxidation catalyst using the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, 2 or 3.
10. An anti-bacterial agent using the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, 2 or 3.
- 20
11. An ion conducting material using the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, 2 or 3.
- 25
12. An electrode for a solid-electrolyte fuel cell using the  $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$  compound according to Claim 1, 2 or 3.
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- 50
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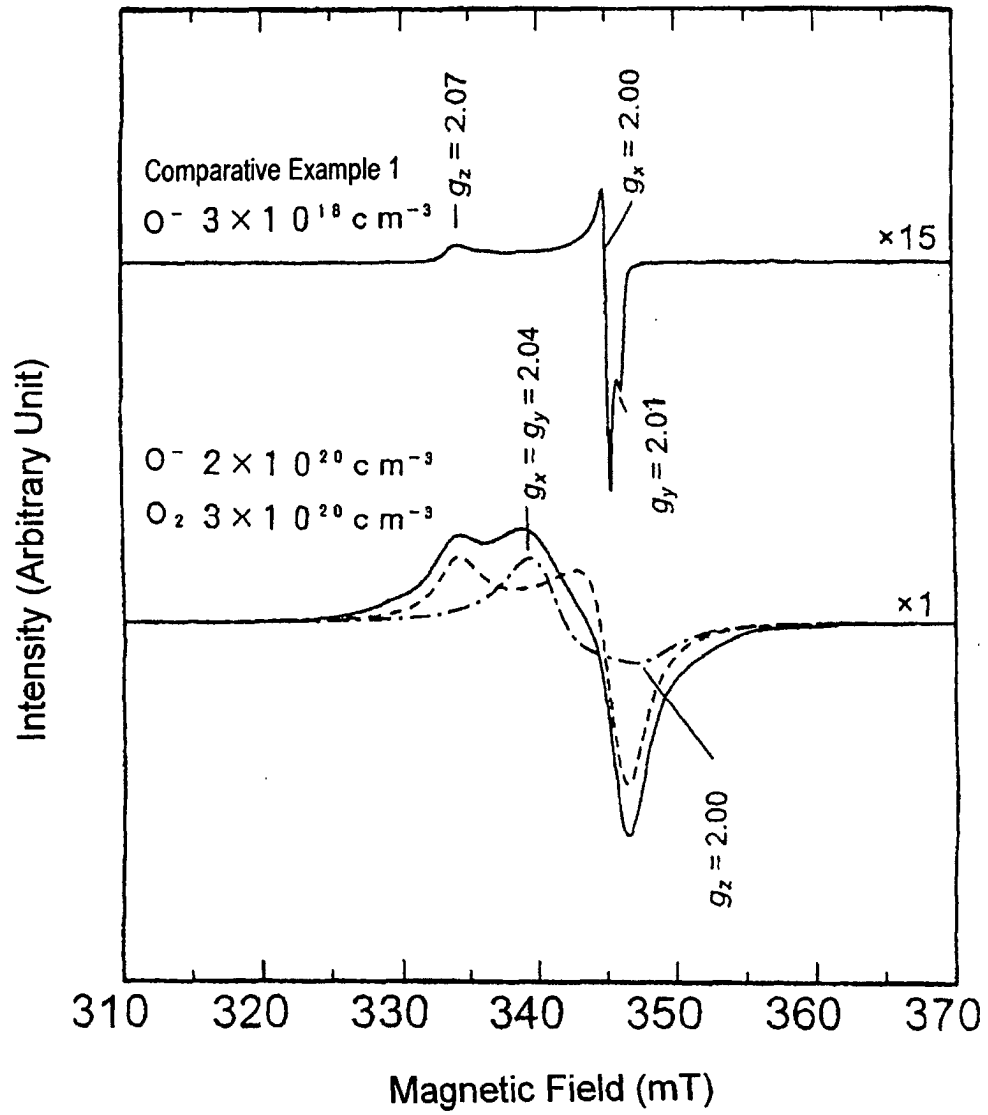
**Fig. 1**



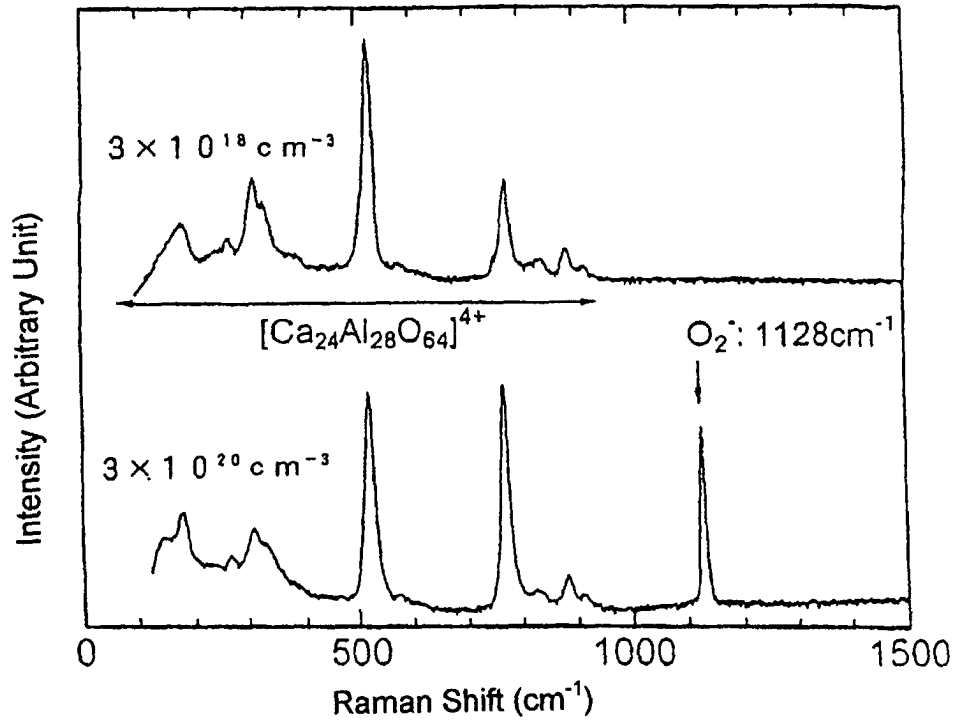
**Fig. 2**



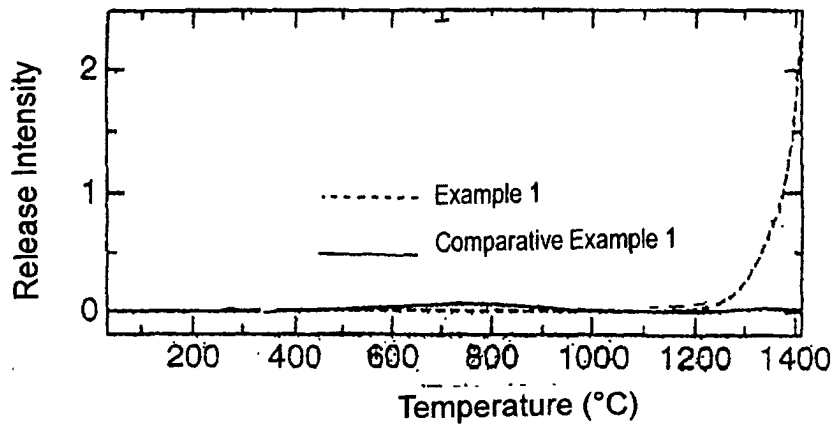
**Fig. 3**



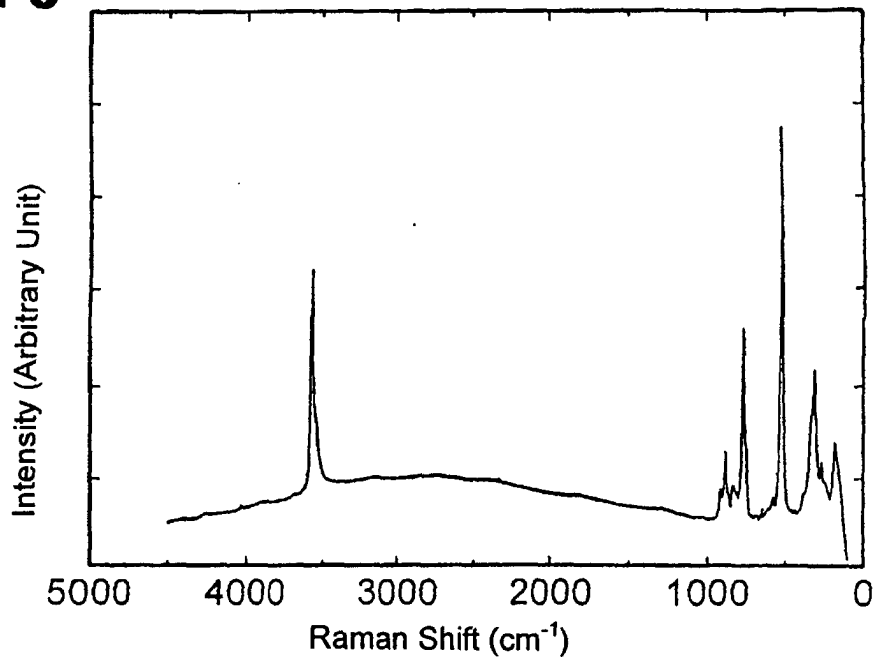
**Fig. 4**



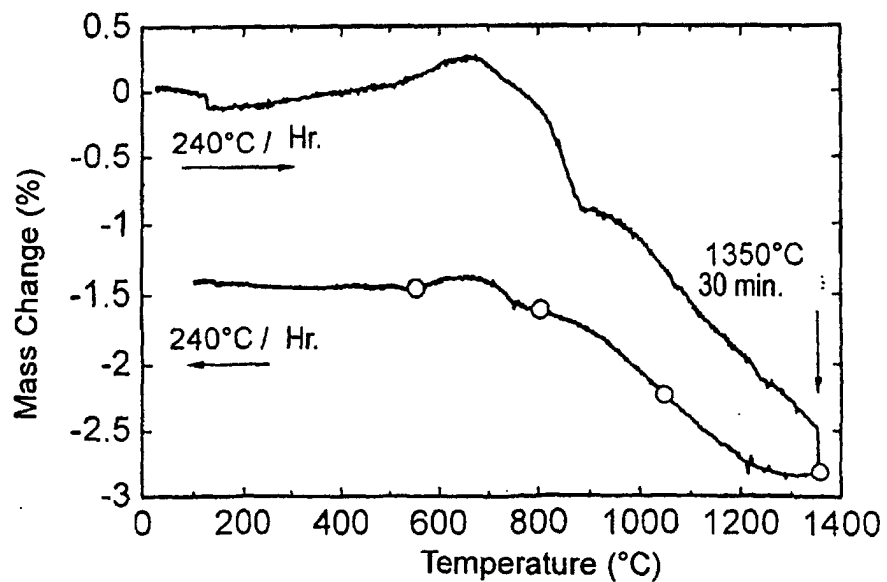
**Fig. 5**



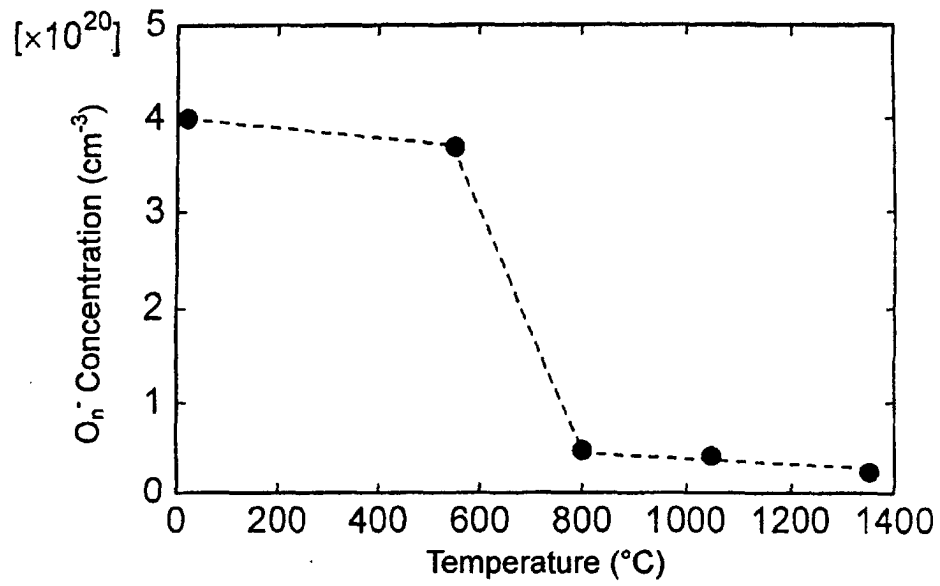
**Fig. 6**



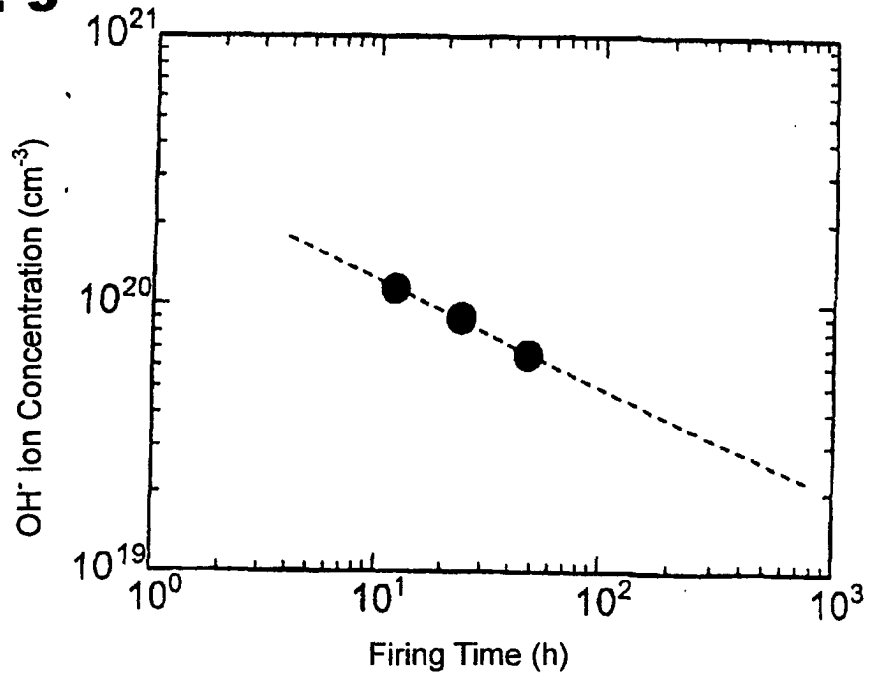
**Fig. 7**



**Fig. 8**



**Fig. 9**



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/10806

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> Int.Cl <sup>7</sup> C01F7/16, B01J23/02, G01N31/00, A01N59/06, H01B1/06, H01B1/08, H01M4/86  According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) Int.Cl <sup>7</sup> C01F7/16, B01J23/02, G01N31/00, A01N59/06, H01B1/06, H01B1/08, H01M4/86  Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1926-1996 Toroku Jitsuyo Shinan Koho 1994-2002 Kokai Jitsuyo Shinan Koho 1971-2002 Jitsuyo Shinan Toroku Koho 1996-2002  Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI, CA		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JOURNAL OF SOLID STATE CHEMISTRY, Vol.81(1989), R. STOBER, et al., "Paramagnetic Monitors (Mn <sup>2+</sup> , Mn <sup>4+</sup> , Fe <sup>3+</sup> , and O <sup>2-</sup> ) in the Solid State Reaction Yielding 12CaO·7Al <sub>2</sub> O <sub>3</sub> and Other Aluminates", pages 152 to 164	1-5, 8 6, 7, 9-12
X Y	INORGANIC CHEMISTRY, Vol.26, No.8(1987), HIDEO HOSONO, et al., "Occurrence of Superoxide Radical Ion in Crystalline 12CaO·7Al <sub>2</sub> O <sub>3</sub> Prepared via Solid-State Reactions", pages 1192 to 1195	1-5, 8 6, 7, 9-12
A	Journal of the Material Science Society of Japan, Vol.33, No.4(1996), Hideo HOSONO, Maboroshino Kagakushu "Cho Sankabutsu Ion Radical" o Konodo ni Hosetsusuru Kessho: 12CaO·7Al <sub>2</sub> O <sub>3</sub> , pages 171 to 172	1-12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 25 November, 2002 (25.11.02)		Date of mailing of the international search report 10 December, 2002 (10.12.02)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP02/10806

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CHEMICAL ABSTRACTS, Vol.74, No.16, 19 April, 1971 (19.04.71), (Columbus. Ohio. U.S.A.), IMLACH, J.A., et al., "Excess Oxygen and the stability of $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ ", page 191, left column; Abstract No. 79160m Cem. Concr. Res. (1971), pages 57 to 61(Eng)	1-12
P,X	WO 01/79115 A1 (Japan Science and Technology Corp.), 25 October, 2001 (25.10.01), Abstract; Claims 1 to 3, 7 to 10 & JP 2002-003218 A	3,5,8-12

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