

(D-2) to form a gel, and drying, molding and then sintering the gel;

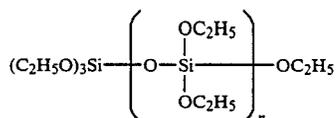
(D-1): at least one kind of ceramics fine particles having a composition different from a sintered body obtained from components (A) to (C) or having a crystal different from crystals formed in the sintered body,

(D-2): ceramic short fibers and/or whiskers.

The invention also provides a novel  $\text{SiO}_2$ — $\text{P}_2\text{O}_5$ — $\text{CaO}$  glass or glass-ceramic composite sintered body containing component (D-1) and component (D-2).

#### Preferred Embodiments of the Invention

As silicic acid esters represented by the general formula (I) as used in the invention, those wherein  $\text{R}^1$  to  $\text{R}_4$  are  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $\text{iso-C}_3\text{H}_7$ ,  $n\text{-C}_4\text{H}_9$  or  $-\text{C}_2\text{H}_4\text{OCH}_3$  in the formula (I) are preferable, and among these those wherein  $\text{R}^1$  to  $\text{R}_4$  are the same group are particularly preferred. In the invention, those wherein  $n$  is 0 are preferable, and those wherein  $n$  is 1 to 10 are also preferable. Specific examples of silicic acid esters represented by the general formula (I) include tetramethoxysilane, tetraethoxysilane, tetra( $n$ -propoxy)silane, tetraisopropoxysilane, tetrabutoxysilane, tetra(2-methoxyethoxy)silane, and oligomers (2 to 10 monomers) of these silicates. Of these examples, tetraethoxysilane  $\text{Si}(\text{OC}_2\text{H}_5)_4$  can be readily obtained as Ethyl Silicate 28 from Colcoat Co., Ltd. and a 5-mol-average condensation product of tetraethoxysilane:



$n = 4$

can also be obtained as Ethyl Silicate 40 from Colcoat Co., Ltd. The above silicic acid esters can be used alone or in combinations of two or more of them.

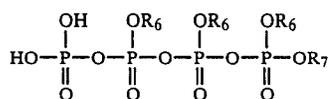
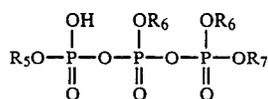
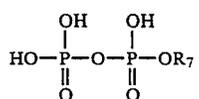
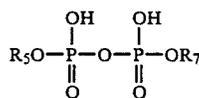
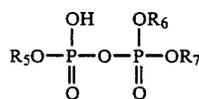
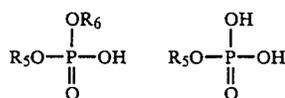
The concentration of silicic acid esters in the reaction mixture can be optionally changed, but is preferably 0.1 to 40 weight % (hereinafter abbreviated as %), particularly preferably 2 to 30% in terms of  $\text{SiO}_2$  amount in the reaction mixture of matrix components except components (D-1) and (D-2).

As the phosphorus compound in the invention there can be used one compound represented by the general formulae (II), (III) and (IV) or a mixture of two or more of them.

As phosphoric acid esters of the formula (II), those wherein  $\text{R}_5$  to  $\text{R}_7$  are alkyl groups having 1 to 4 carbon atoms in the formula (II) are preferable, and those wherein  $\text{R}_5$  to  $\text{R}_7$  are phenyl groups or benzyl groups are also preferred. Further,  $m$  is preferably 0 to 4. Further, phosphoric acid esters wherein all of  $\text{R}_5$  to  $\text{R}_7$  are alkyl groups, phosphoric acid wherein all of  $\text{R}_5$  to  $\text{R}_7$  are hydrogen and condensates thereof, and partial esters containing both alkyl group(s) and hydrogen can all be used. Further, in phosphorous acid and phosphorous acid esters represented by the general formulae (III) and (IV), as the alkyl group those having 1 to 4 carbon atoms are preferable, and a phenyl group and a benzyl group are also preferable. Specific examples of preferred compounds include those wherein  $\text{R}_5$  to  $\text{R}_9$  are

methyl, ethyl, iso-propyl,  $n$ -propyl,  $n$ -butyl, phenyl and benzyl in the general formulae (III) and (IV).

Among the above various phosphorus compounds in the invention, most preferable are those of the formula (II) wherein at least one of  $\text{R}_5$  to  $\text{R}_7$  is hydrogen, but all of them are not hydrogen at the same time. As specific examples the following compounds alone and mixtures of two or more of them can be mentioned.



$\text{R}_5$  to  $\text{R}_7$  in the above formulae are the same as  $\text{R}_5$  to  $\text{R}_7$  in the formula (II) except that hydrogen is excluded.

The above partial esters of phosphoric acid can be readily obtained, for example, by partially hydrolyzing the corresponding phosphoric acid esters, by adding phosphoric acids to the corresponding alcohols to carry out esterification, or by reacting phosphorus pentoxide with alcohols and hydrolyzing the product.

Calcium ion can be mentioned as another essential component of the invention, and calcium salts or compounds represented by the above general formula (V) are used as substances forming the ion. These substances are used since addition of Ca is necessary for preparing bio-active glasses or glass-ceramics. Calcium salts include, for example, calcium nitrate, calcium acetate, calcium chloride, calcium hydroxide, calcium hydrogen citrate, calcium citrate and calcium oxalate. Among these calcium components, water soluble salts such as calcium nitrate, calcium acetate and calcium chloride are particularly preferred.

Further, in the invention there can be added besides the above constitutive elements, elements which can become constitutive oxides of gel, namely glass or glass-ceramics which are the matrix of the sintered body. These elements are specifically Li, Na, K, Mg, Al, Zr, Ti, B, etc., and these elements can be used either in the form of metal alkoxides or in the form of soluble salts. These compounds are suitably used in an amount of 0 to 30% in terms of oxide based on the total amount of the oxides when all of gel constituting elements are converted to oxides.