STUDIES ON THE SOL-GEL PROCESSING OF GLASS / CERAMICS

by

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DEDICATED TO MY PARENTS

CERTIFICATE

This is to certify that the thesis entitled *"STUDIES ON THE SOL GEL PROCESSING OF GLASS/CERAMICS"* being submitted by *Mr. VIRENDRA KUMAR PARASHAR* to the Indian Institute of Technology, Delhi for the award of the degree of *Doctor of Philosophy* in Chemistry, is a record of bonafide research work carried out by him. *Mr. VIRENDRA KUMAR PARASHAR* has worked under our guidance and supervision, and has fulfilled the requirements for the submission of this thesis which, to our knowledge, has reached requisite standard. The results contained in this dissertation have not been submitted, in part or in full, to any other university or institute for award of any degree or diploma.

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ABSTRACT

The thesis comprises the studies undertaken to understand the process of gel network formation from alkoxides and processing of advance ceramics viz. zircon, silicon oxycarbide and silicon oxynitride. Applications of the sol-gel process for obtaining oxidation resistant coatings and matrix for chemical sensor and catalyst have also been evaluated.

Studies carried out on the evolution of tetraethylorthosilicate (TEOS) derived silica glasses revealed that the hydrolytic - polycondensation of TEOS is more rapid in dipolar aprotic solvents, (acetonitrile) than in polar protic solvents (ethanol). High molar ratio of H_2O:TEOS (Rw), high concentration of HCl, and catalysis by NH_3 lead to completely polymerized three dimensional network formation. Analysis of the results show that thermal treatment of gels is accompanied with the strengthening of polynetwork in steps. These steps occur at an early stage of drying, after organic burn out and silanol condensation.

Preparation of monolithic silica gels is hindered by the occurrence of cracks. According to the published stuides, cracks can largely be avoided either by very slow evaporation, hyper critical drying or by introducing DCCA (drying control chemical additives) to starting solutions. In the present studies, it was found that the gels produced using DCCA have low density, large pores and high carbon residue. These factors make it unfavorable for the fabrication of engineering products. Main cause for the occurrence of cracking in gels is the presence of water. A new procedure has, therefore, been devised in which the excess amount of water present in the system, which is responsible for the crack formation, is removed by azeotrope formation. This azeotrope formation facilitates the formation of monolith gels by removal of all unwanted species as well as excess water at a lower temperature and consequently enhances the desired properties (high density, high strength and absence of carbon residues) useful for fabrication of engineering products.

The evaluation of mechanical properties {diametral compressive strength (DCS), flexural strength (FS)} of silica reflect the dependence of DCS and FS on the concentration and nature of the solvent used for sol gel processing. Use of acetonitrile as a solvent in place of ethanol helps in increasing the DCS and FS of glasses to 3 fold and 5 fold, respectively. Increase in acetonitrile molar concentration with respect to TEOS from 2 to 20 in the processing medium increases the FS and DCS to 108 MPa and 17 MPa from 27 MPa and 8 MPa, respectively.

X-ray diffraction studies of ZrO_2 -SiO_2 mixed oxide having compositions x ZrO_2 - (100-x) SiO_2 , (x = 10 to 60 weight %) reveal that all the gels contain tetragonal phase of zirconia on heat treatment to 600 ^{0}C. Tetragonal crystalline phase of zirconia is stable in the low zirconia content (upto 40 weight %) binary oxides even on heat treatment to 1100 ^{0}C. FTIR spectroscopy along with X-ray diffraction studies are indicative of the formation of Si-O-Zr linkages in the silica- zirconia binary oxide.

Nitridation of silica reveals the incorporation of nitrogen into the silica network. Nitridation of copolymer gels (MTEOS-TEOS and DMDEOS-TEOS) results in the development of an oxidation resistant material having SiO,N/C present in them, composition of which depends upon the amount of alkyl substituted silicon alkoxide used. However, a thermally stable silicon oxycarbide glass is produced on sintering the copolymers in argon atmosphere.

Application of sol gel processing studied during present work includes sol gel derived oxidation protective coatings on carbon materials. Preliminary investigations on the oxidation resistance of coated C/C composites reveal that application of coatings effectively increases the oxidation inhibition temperature upto 1000 °C.

Sol-gel derived silica gel serves as a solid support to incorporate the analytical reagent and metallic catalyst in the gel network. Doped sol gels are analytically efficient in the estimation of nitrite in solution and nitrogen dioxide in air (gases). Catalytic activity of Pt doped gel is excellent in the hydrogenation of cyclohexene.

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