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Effect of APC addition on precursors properties during synthesis of B_4C nano powder by a sol–gel process

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ABSTRACT

In this study different characteristics regarding to dispersion of a suspension containing precursor particles with respect to charge, particle size and rheological measurements were investigated. Ammonium poly carboxylate (APC) was used here as a dispersing agent. From our investigations it was exhibited that point zero charge (PZC) for precursor particles is about 6.5–7. On the other hand, it was revealed that surface charge of precursor particles was changed significantly in presence of ammonium poly carboxylate agent, and also PZC amounts shifted toward lower acidic pHs in the range of 4.04–4.4. From electrokinetic data, adsorption specific free energy (ΔG^0_{sp}) between superficial sites and adsorbing poly electrolytes (APC) were measured and it was found that ΔG^0_{sp} has a negative amount (equivalent to $-3.1181RT$) in presence of dispersant agents. In presence of APC dispersant agent particle size can be designed to the range of less than 10 nm. From rheometerical measurements performed on a sol containing precursor particles revealed that in mean pH ranges sol viscosity rises and finally particles will show less stability. FTIR analysis from gel powder sample showed existence of B–O–C bonds formed during hydrolysis and condensation reactions. XRD investigations on sintered powder at 1270 °C revealed that final product mainly was composed of B_4C phase. Raman spectroscopy was employed to support the results of B_4C formation. TEM analysis exhibited that B_4C particle size was in the range of 20–40 nm and formed particles are polycrystalline with homogenous morphology.

1. Introduction

Boron carbide (B_4C) is one of advanced ceramics with outstanding properties. These unique characteristics make boron carbide more interesting than other ceramic carbides. Among these properties are high neutron adsorption, low density, high hardness (close to that of diamond), and high chemical and wear resistance [1–4]. This ceramic material is mostly used in military industry as body armors, in electronics as thermocouples, in nuclear power plants as an absorber for neutron radiation, and also for wear applications for example as nozzles for abrasive slurries [5–7]. Various experimental and industrial methods were utilized in order to synthesize boron carbide such as carbothermal reduction [8]; but chemical methods are more preferable because they can give high homogeneity in molecular level which is of great importance in production of advanced ceramic parts. Chemical methods are accurate procedures which can provide possibility to produce powder ceramics in submicron levels without agglomeration. Among these methods, sol–gel is a unique one for synthesis of nanometric particles. This method has some advantages including high purity of products [9], high chemical activity, powder sinter ability and finally it provides possibility for precursors to be mixed at molecular levels. Using alkoxides as precursors in sol–gel for nano powder synthesis is so popular, since by suitable selection of them an ideal powder having outstanding properties such as high purity and chemical homogeneity can be yielded [10]. So in this study we tried to control our final powder properties such as particle size, high purity and homogeneous morphology accurately by the means of suitable selection of alkoxides as boron precursors and also synthesis process variables. Accordingly, Soraru et al. have used boron alkoxides as precursor in borosilicates glasses production [11].

Dispersion of colloidal nanometric suspension in aqueous and non-aqueous systems is key step for many of modern synthesis processes. Holding a nanometric system in the form of separate molecular components is so difficult and these components always tend to come together and form firm agglomerates. As a general trend colloidal suspensions and nano particles are unstable which comes from their high level of surface energies; nevertheless, in such a system kinetic stability can be provided by making an energy barrier against agglomeration. To achieve this goal we utilize electrical double layer or electrostatic forces [12]. By the means of polymeric additions that can be ionized in water, stable suspen-

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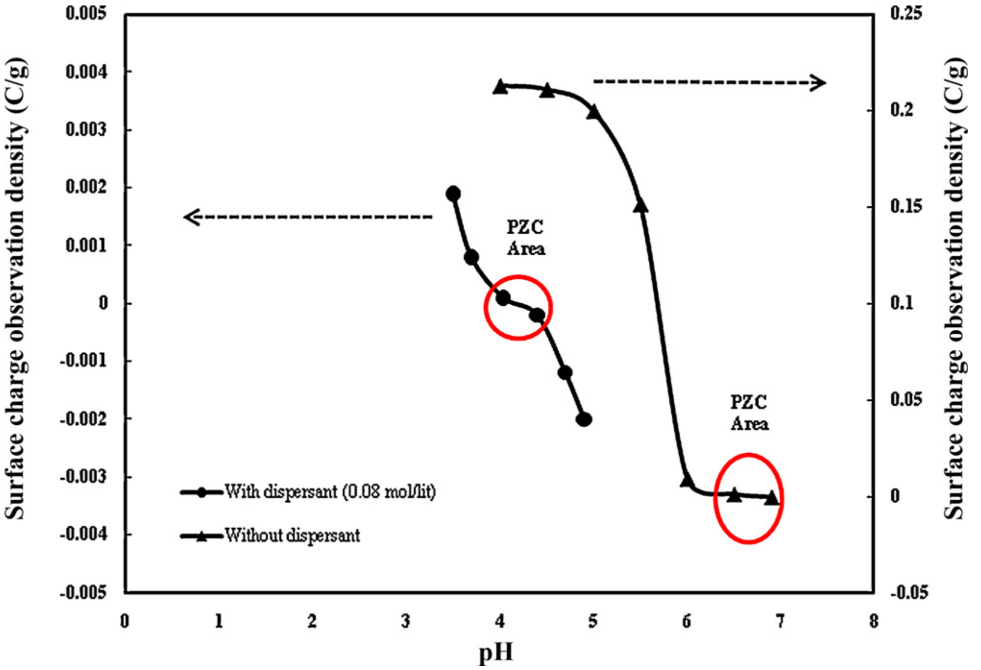

Fig. 1. The effect of pH on surface charge density with and without dispersant.

sions can be formed by which size of different particles such as SiC [13] can be thoroughly designable in the sol. Here we will follow a similar procedure to control particle size of B and C elements in the sol by addition of specific compounds.

Sinha et al. have synthesized boron carbide powder by the means of a carbothermal reduction process. They used boric acid and citric acid as precursors. The final product was composed of nearly equiaxial particles which showed a narrow size distribution with average of 2.25 μm [14]. Chen et al. synthesized boron carbide nano particles by reaction of boron, which was produced as a result of magnesium diboride thermal decomposition, with carbon multi layer nanotubes at 1150 °C after 3 h in vaccum [15]. Chang et al. reported synthesis of boron carbide particles in a high temperature furnace reactor. They used a mixture of amorphous carbon and amorphous boron and heated it up to 1550 °C and in this way boron carbide product was synthesized with an average particle size of 200 nm which varied in the range of 50–350 nm [16].

In this study dispersion behavior of nanometric precursor particles in presence of ammonium poly carboxylate was investigated. The main aim of this study was to optimize sol properties and also to control precursor particles size in a way that no agglomeration will occur, and as a result a nanometric B_4C powder with uniform morphology could be synthesized.

2. Experimental

Initial chemicals which were used in this study was included of tetramethylborate (TMB, Merck Ag Germany), chloridric acid, NaOH (HCl, NaOH, Merck Ag Germany), dimethylformaldehyde (DMF, Merck Ag Germany), phenolic resin (Resol, RIL 800, Resitan Co, Iran) and distilled water.

Ammonium poly carboxylate (APC, D-305) was used as dispersant agent which has an average molecular weight equals to 8000–10,000 g/mol. Ammonium poly carboxylate structure and possible decomposition reactions show that functional groups which acts here are acidic carboxyl groups (–COOH) which can be decomposed into COO^- and H_3O^+ (reaction (1)) [12].

$$RCOOH + H_2O \rightarrow RCOO^- + H_3O^+ \quad (1)$$

At first, 50 g of phenolic resin were dissolved in 100 ml dimethylformaldehyde (DMF) and 80 ml trimethylborate was added to this. Afterwards, 30 ml distilled water was also added to last mentioned solution, regularly. The resulted solution was stirred under flux conditions by a magnetic stirrer till a very uniform and homogeneous solution was formed. In order to establish sol stability specific amount of surface activator (APC) was added to the sol. Subsequently, after completion of hydrolysis reactions $B(OH)_3$ particles were formed into the sol. So our final sol is composed of $B(OH)_3$ and resin phenolic which were thoroughly dissolved in it. With heating up the sol and over time particles link together as a result of condensation reactions and polymers with (=B–O–B=) bonds form. This polymer has an integrated chain structure in which liquid phase is trapped. The carbon phase is homogenously dispersed in polymeric structure at molecular levels. Finally, we will obtain a Xerogel by drying of the resulted gel. In order to remove structural water and inorganic materials from our gel powder, it was heated up to 600 °C for 1 h under Ar atmosphere. Then, pyrolyzed powder was heat treated in an electric furnace (Carbolite1600) under Ar atmosphere with a flow rate of 80 ml/min at 1270 °C for 2 h.

Rheometric analysis (Physica, Mcr800) was performed from ambient temperature up to 120 °C. During this analysis viscosity was measured at constant temperature of 25 °C with shear rate of 2600 s^{-1}. Rheological behavior of the suspension containing precursor particles was investigated by determining viscosity and also shear stress as a function of shear amount and sol's pH. A particle-charge detector (Zetasizer, Malvern DTS) was used to measure surface charges of precursor particles. PCD works on the basis of measurements of current potentials which are resulted from partial separation of opposite ions in double layer from charged particles in liquid flow. Dynamic light scattering (DLS, Malvern DTS) was used in order to analyze particle sizes and stability of our colloidal system. This method deals with suspended particles which move on the basis of Brownian motions in sol and the relation between particle size and their mobility can be estimated according to Stokes–Einstein formula (Eq. (2)) [17].

$$\mu_p = \frac{1}{6\pi\eta r} \quad (2)$$

FTIR (FTIR, SHIMADZU 8400S) was used in order to characterize present bonding types for powder sample synthesized by sol–gel process. The wavenumbers for FTIR analysis were in the range of 400–4000 cm^{-1}. The structural analysis and average crystallite size measurements for synthesized powder were done using X-ray diffractometer (XRD, Philips Xpert) by Cu Kα radiation (λ = 1.54 Å). Raman spectrum was measured on Almega Thermo Nicolet Dispersive Raman spectrometer. The 532 nm laser was employed as an excitation light source. Transmission electron microscopy (TEM, Philips CM200) was used for agglomerates size investigation as well as both quantitative and qualitative analysis and for determination of size, shape and particles distribution in synthesized powder, respectively.

3. Results and discussion

3.1. Surface chemical properties of precursor particles

Stability for a suspension containing precursor particles is strongly related to their surface charges. When boron alkoxides are

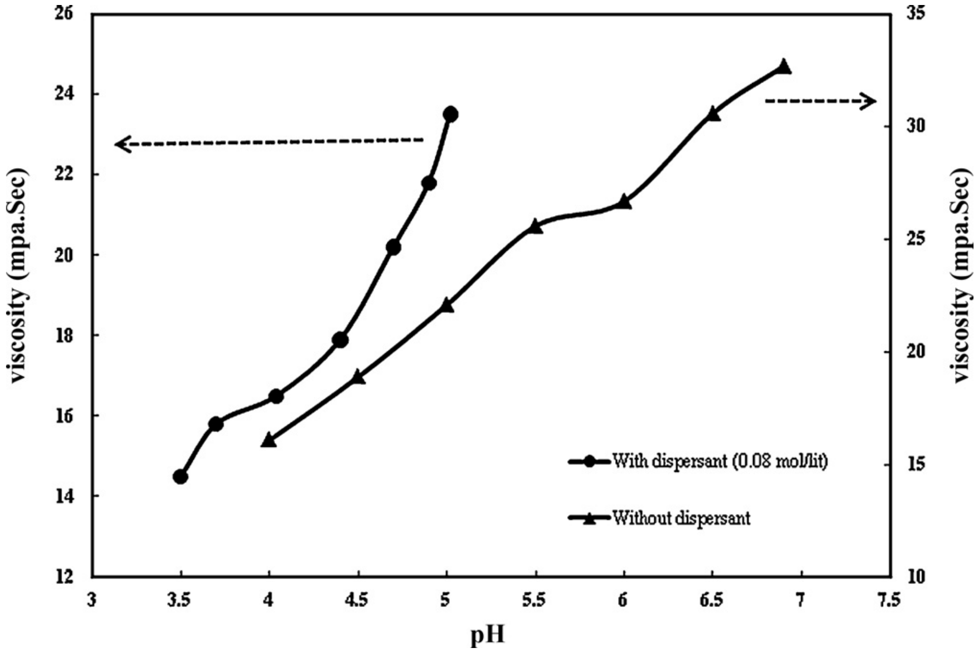

Fig. 2. Effect of pH on suspension viscosity.

exposed to water molecules, they undergo hydrolysis according to reaction (3) and so OH groups will be replaced by OR groups.

$$\text{B–OR} + H_2O \rightarrow \text{B–OH} + \text{ROH} \tag{3}$$

In this reaction B–OH groups are involved which are amorphous. According to reactions (4) and (5), these groups react with H^+ ions in pHs lower than PZC and form (B–OH_2^+). These groups react with OH^- ions in the pH ranges over PZC and form (B–O^-) groups [18].

$$\text{B–OH} + H^+ \rightarrow \text{B–}OH_2^+ \quad \text{pH} < \text{PZC} \tag{4}$$

$$\text{B–OH} + OH^- \rightarrow \text{B–}O^- + H_2O \quad \text{pH} > \text{PZC} \tag{5}$$

Table 1 summarizes charge creation in different pH amounts which occurs according to (4) and (5) reactions.

As it can be seen, precursor particles in pH range of 6.5–6.9 have only PZC and as pH increases the surface charge amount becomes more negative. This findings show that B–OH bonds tend to acidic pH conditions and we can gain a lower pH amount by addition of an intermediate agent; hence, aggregation can be decreased. To obtain suspension with high particle dispersion we should establish a repulsive electrical force among particles.

Fig. 1 shows surface charge variations (C/g) as a function of pH with and without a dispersant agent.

It demonstrates that PZC amount for B–OH functional groups occurs in the pH range of 6.5–6.9 and suspended particles in sol have positive and negative charges in pHs less or more than this range, respectively. By addition of suitable amount of APC dispersing agent (here 0.08 mol/l) to the sol, surface charge and pH change. It occurs as a result of surface charge increase which is caused by adsorption of poly electrolytic dispersing agent on the surface of precursor particles which in turn causes pH_{PZC} level to shift toward lower amounts in the range of 4.04–4.4. So interaction between precursor particles and dispersing agent probably has chemical nature and shift the pH amount toward more acidic conditions. Chemical adsorption process, which occurs by formation of chemical bonds, mostly is known as a reversible adsorption process. This process causes a change in relative intrinsic energy and also shifts PZC amount.

Table 1
Experimental data of nanosize particles surface charge density.

pH	Surface charge observation density (C/g)	
4	0.2131	
4.5	0.2111	
5	0.2	
5.5	0.1516	
6	0.0091	
6.5	0.001	pH_{PZC} = 6.5–6.9
6.9	−0.0006	
7.5	−0.2006	

3.2. Rheological measurements

Fig. 2 shows viscosity amounts for a sol containing precursor particles as a function of pH in constant shear rate of $2600\,s^{-1}$.

As it is seen from the picture in acidic pH ranges, the closer pH amount is to 7, the more viscosity we will see for the sol; therefore, the highest viscosity is observed for PZC point. In other word, as viscosity increases, the attraction between particles in sol also increases and so sol mobility decreases. According to Eq. (2) at a constant temperature, sol mobility and its stability decreases as viscosity increases. By addition of APC sol viscosity can be decreased as it can also be observed in above figure. For extremely low or extremely high pHs, suspension shows a good dispersion behavior, so sol viscosity gets low and as a result particles mobility increases and resulting sol will become more stable.

3.3. Sol stability

Zeta potentials for a sol containing precursor particles are shown in Fig. 3.

As it can be concluded from zeta potential data, particles in sol are unstable and they can easily join together. The highest amount for zeta potential happens in low pH (<5) equals to 15 mV which is a very low potential. At PZC zeta potential is equivalent to 5.5 mV and the sol is at its lowest stability at this point. So, addition of an intermediate agent into the sol is necessary in order to prevent agglomeration under acidic conditions.

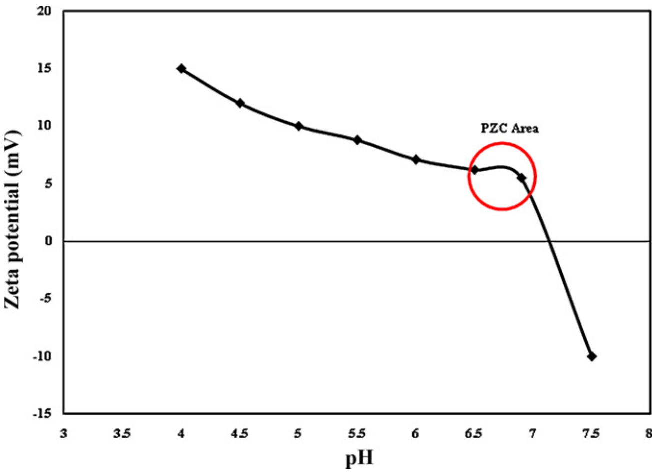

Fig. 3. Zeta potential variation vs. pH.

3.4. Calculation of adsorption specific free energy by electrokinetic data

It is well proved that double layer interaction plays an important role in adsorption of agents on the surface. One of the most important methods for investigation of interactions between adsorption agents is electrokinetic measurements which are preformed on a sol containing surface activators. Electrokinetic data for systems in which chemical absorption occurs show that surface charge on particles changes as a result of addition of surface activators. The reason for this change can be explained according to specific interactions occurring between surface sites and surface activator agents, and also according to Eq. (6) on the basis of electrical double layer theory [12]. These specific interactions are along with surface charge variations which in turn are related to ΔG^0_{sp}.

$$\Delta G^0_{sp} = -RT(\ln \Delta pH - \ln C_o - \ln 1.0396) \tag{6}$$

where, ΔG^0_{sp} is the free energy of interaction between particles surface and dispersant, ΔpH is sol pH changes due to dispersant addition, C_o is the dispersant concentration (0.08 mol/l) and R and T are standard coefficient of gas and temperature (K), respectively.

Table 2 summarizes specific free energy for superficial interactions in different pH amounts.

It can be seen that the more negative ΔG^0_{sp} is, the more effective is reaction between particle surface and dispersing agent, but on the other side electric repulsion for double layer will increase, too. Surface charge change in presence of polyelectrolyte with chemical absorption mechanism can be determined for interaction specific free energy (ΔG^0_{sp}) to some extent and dispersibility then can be related to variations of interaction free energy.

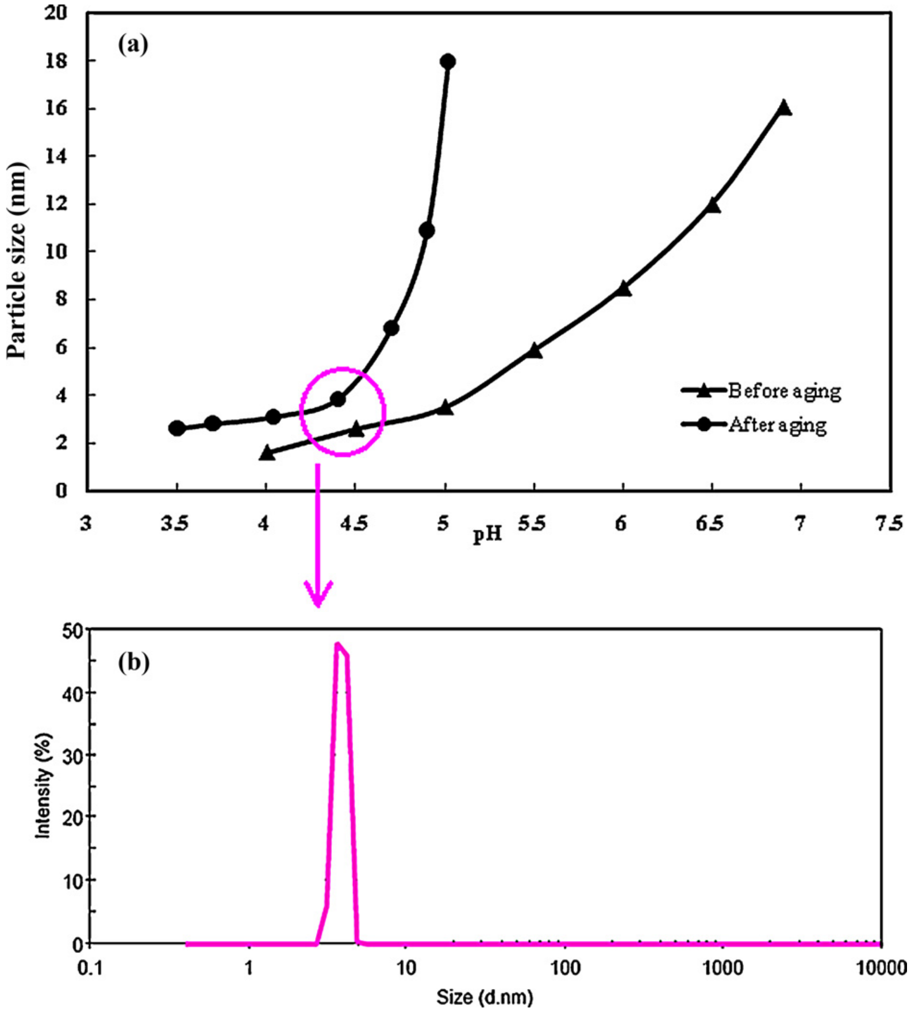

Fig. 4. The effect of pH on particles size.

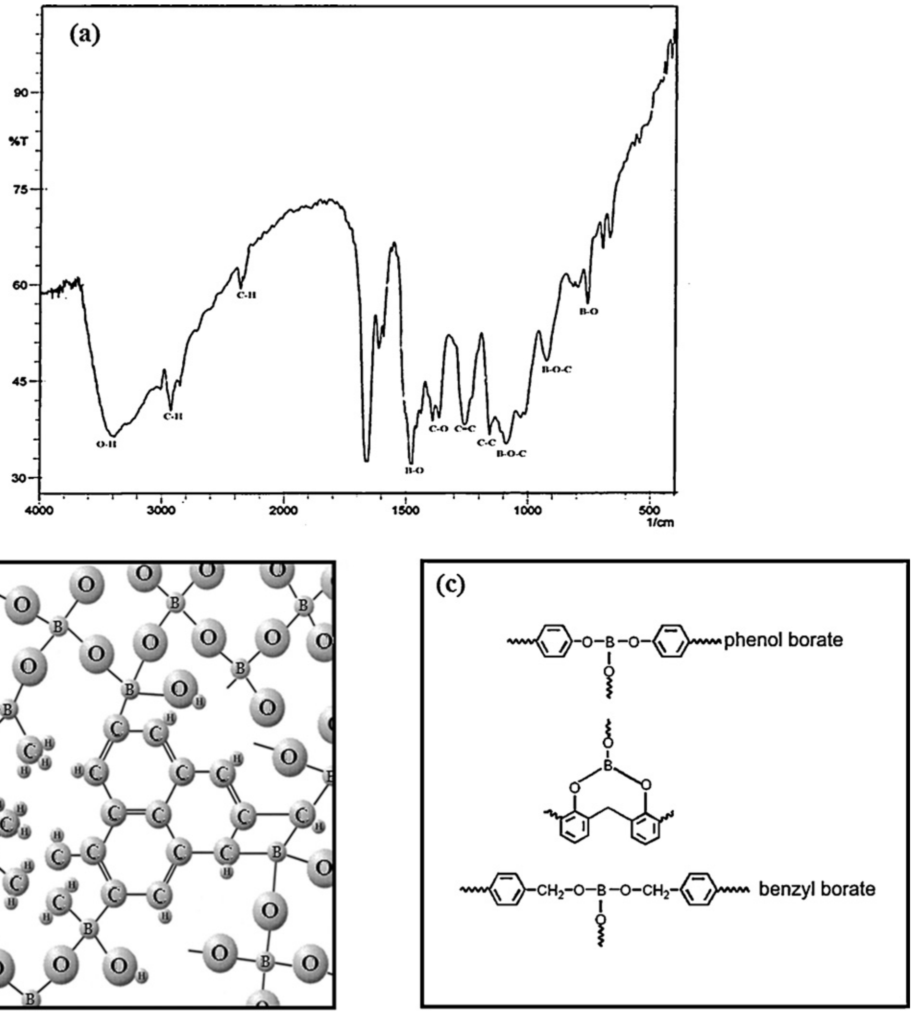

Fig. 5. (a) FTIR spectrum of gel powder and (b, c) schematic of B–O–C bonds.

3.5. *Investigation of precursor's particle size in the sol*

Fig. 4 shows particle size variations in the sol and size distribution.

As it is seen from the picture (Fig. 4(a)) under acidic conditions and for low pH amounts, particles are finer, since in this pH range concentration of OH^- ions is very low and it does not allow the reaction (3) to progress completely. So as a result of low solubility rate, hydrolysis reaction progresses very slowly in this range of pH; but for high pH values concentration of OH^- ions increases and along with particles formation growth also occurs and they become bigger over time. Although, in aqueous systems precursor particles are under an electrostatic repulsive force which is caused by double layers surrounding them, but in order to prevent agglomeration in atomic levels organic materials also can be used to thicken adsorption layers which leads to electrostatic stability. Electrostatic stability is caused by two basic repulsion forces, electrostatic and electrosteric forces, which are formed during adsorption of charged polymers on particles surface. After long time needed for sol to be prepared an attraction force also is formed between particles as a result of electric charge reduction and thinning of double layer; consequently agglomerates form which means we will have larger particles. Electrostatic forces caused by polymer adsorption on particles surface brings about a higher zeta potential and finally it causes an electric repulsion between particles. By addition of APC as dispersing agent, in amount of 0.08 mol/l, into the sol makes particles more stable mostly in pH range of 5–7. Fig. 4(b) shows particle size distribution for pH = 4.4 in presence of APC agent. A narrow size distribution with mean value of less than 10 nm is observable for particles in this picture, and no dispersion has occurred in the sol.

Table 2
Specific free energy of interaction between particles and APC.

ΔG^0_{sp} (unit *RT*)	ΔpH	pH	
		No dispersant	Sol/APC
−1.7938	0.5	4	3.5
−2.2637	0.8	4.5	3.7
−2.4460	0.96	5	4.04
−2.5822	1.1	5.5	4.4
−2.7492	1.3	6	4.7
−2.9568	1.6	6.5	4.9
−3.1181	1.88	6.9	5.02

4. Powder properties

The FTIR spectrum and schematic of B–O–C bonds are shown in Fig. 5 for gel powder sample.

From Fig. 5(a), a broad band observed at 3200 cm^{-1} corresponds to stretching vibrations of –OH functional groups. There is another adsorption band located around 1030 cm^{-1} caused by B–O–C bonds

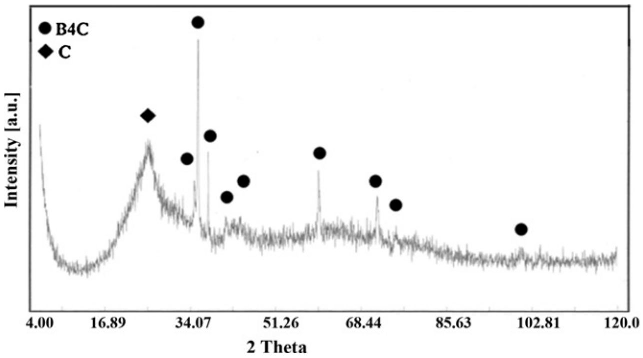

Fig. 6. X-ray diffraction pattern of synthesized B_4C nano powder at 1270 °C.

[19]. Around 2950 cm^{-1} there is a band related to (C–H) bonds of methylene which keep phenol's aromatic rings in phenolic resin together [20]. The band appears around 1470 cm^{-1} is corresponded to stretching vibrations of B–O bonds. Other bands seen in the range of 1150–1450 cm^{-1} and 1500–1700 cm^{-1} are related to phenolic resin bonding groups including C–C, C–O and C=C, and phenol groups of carbonic phase, respectively.

Therefore, it is concluded that during sol preparation process, sufficient interactions between tetramethylborate and phenolic resin precursors were made at molecular levels and B–O–C bond (Fig. 5(b) and (c) [21]) was formed at around 1030 and 900 cm^{-1}.

Fig. 6 shows the X-ray diffraction pattern of synthesized powder heat treated at 1270 °C for 2 h.

It can be seen that main peaks of synthesized powder can be corresponded to *d*-spacing amounts of rhombohedral B_4C phase from database. The amounts we have got here for lattice constants (a = 5.603 Å and c = 12.08 Å) are so close to experimental equivalents reported for B_4C (a = 5.60 Å and c = 12.08 Å, respectively, JCPDS card, 350798). It should be noted that there is a weak peak around $2\theta = 25°$ which is caused by carbonic phase. Free carbon amounts in final product means that there are still part of precursors remained in our system and part of boron was reacted with carbon during carbothermal reduction.

Sinha et al. [14] synthesized B_4C micro powder at temperature of 1450 °C via simultaneous chemical and carbothermal reduction methods. XRD patterns of the powder showed the presence of free carbon during the synthesis process at the above-mentioned temperature range.

Complementary data about the formation of B_4C can be obtained from Raman spectroscopy. Fig. 7 shows the Raman spectrum of as prepared nano powder. In this spectrum three wide bands located at 705, 802 and 1035 cm^{-1} Raman shift can be clearly indexed to rhombohedral boron carbide along with two double narrow bands at 481/559 cm^{-1}. Also two bands at 1347 and 1630 cm^{-1} attributed to D and G bands of semi crystalline residual carbon in the powder, respectively.

Fig. 8 shows transmission electron micrograph along with its diffraction pattern and EDS spectra under above mentioned conditions of the synthesized powder.

As it is indicated, the mean size of the particles is between 20 and 40 nm with a uniform morphology. As the diffraction pattern shows, synthesized B_4C particles are polycrystalline and so fine. Additionally, from the EDS spectra, it can be seen that synthesized powder has high purity; no additional elements present in it and B and C are dispersed uniformly into synthesized powder which is in good agreement with XRD analysis.

Particle size and morphology of powder could be controlled by time and temperature at heat treatment step. In current research we concluded that the optimum circumstances of B_4C crystallization are temperature of 1270 °C and time of 2 h.leaving this

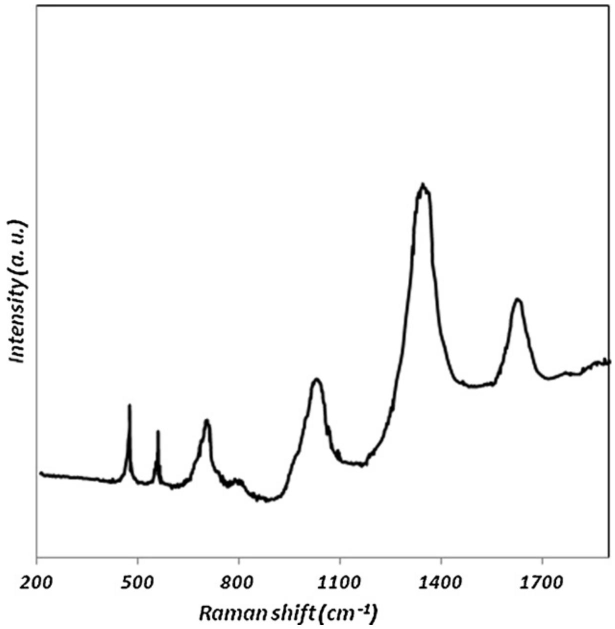

Fig. 7. Raman spectrum of as prepared B_4C nano powder.

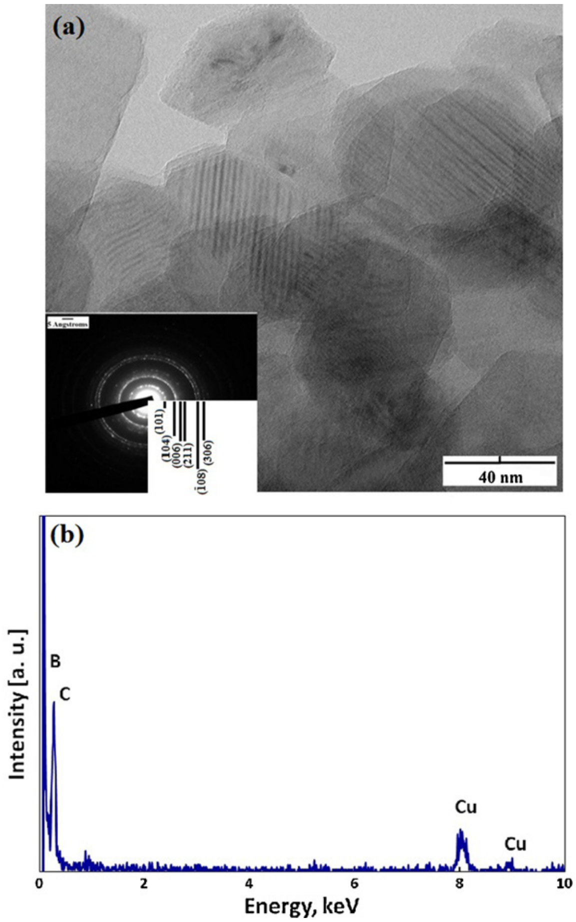

Fig. 8. (a) Transmission electron micrograph and (b) EDS spectra of synthesized B_4C nano powder heat treated at 1270 °C.

optimum circumstances would result in morphology change from powder to whisker state.

5. Conclusion

The effects of involved parameters on stability of suspension containing nanosize precursor particles have been studied in this study. The results showed that the surface charge of nanosize particles in presence of APC dispersants tends to acidic pH ranges less than 4.04–4.4 which means there is a wide range available for composition process. We could well optimize between APC amount and precursors present in the sol which can be concluded from negative values obtained for ΔG^0_{sp} (equals to $-3.1181RT$). Rheological measurements showed that viscosity of the sol was increased at intermediate pH range and decreased at extremely high and extremely low pHs. The particles size could be controlled to less than 10 nm in the presence of APC as a dispersant. The TEM results showed a size in the range of 20–40 nm for synthesized polycrystalline powder with uniform morphology.

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