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SPECIAL FEATURE

Effect of post-sinter annealing on the properties of ceramics

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Sintering has been the most conventional way of fabrication of ceramics. However, it has been observed that sintering can induce compositional inhomogeneity, formation of secondary phases, formation of defects, internal stresses etc. Even though post fabrication annealing has been a key process for bringing about the compositional homogeneity and relieving the internal stresses in metallic systems it remained ignored by and large in ceramics systems. However, in recent times (in last 10–15 years), there have been sizable attempts to correlate effects of post sinter annealing on various properties of ceramics. Since ceramics are used for niche electrical, mechanical, optical and thermal applications it has been attempted to summarize the effect of post sinter annealing on the above properties in this article.

Ceramic materials have been used for many technological applications and their technological significance in modern era continues to grow. Conventional method of fabricating ceramic components includes ceramic powder synthesis followed by green processing and finally sintering. The sole focus pertaining to ceramic processing has been improvement in the densification via optimization of sintering parameters conventionally and then, correlating the sintering parameters to the properties achieved. Most of the research articles available in the literature are silent about the compositional inhomogeneity, formation of secondary phases, formation of defects, generation of internal stresses, etc. during sintering and its subsequent effect on properties. Post fabrication annealing has been a key process to relieve internal stresses and bring about the compositional homogeneity in metallic systems but it remained ignored by and large in ceramics systems. However, in recent times (in last 10–15 years), there have been sizable attempts to correlate effect of post sinter annealing on various properties of ceramics. Since, ceramics are used for niche electrical, mechanical, optical and thermal applications we have attempted to summarize the effect of post sinter annealing on the above properties in this article. Since, the term sintering encompasses various processes like pressureless sintering, vacuum sintering, microwave sintering, spark plasma sintering, hot pressing etc.; effect of annealing on various properties of ceramics after they have been sintered by one of these methods is discussed in the article [1–15].

Electrical properties

Ceramics have been in use for various electrical applications like dielectrics, ferroelectrics, piezoelectrics, conducting applications, and therefore tuning the properties of these ceramics in line with the desired application is necessary to optimize the performance of these materials. Optimization of sintering parameters has been a key subject of research while studying the electrical behavior of ceramics for years. However, literature correlating the effect of post sinter annealing on the electrical properties of ceramics is relatively scarce. Despite that we have dug out following factors which need to be taken into consideration while studying effect of post sinter annealing on the electrical properties (electrical conductivity, dielectric behavior, ferroelectricity, piezoelectricity).

(a) concentration of secondary phases, (b) grain size, (c) density of ceramics after annealing, (d) composition of grain boundary layer, (e) release of internal stresses, (f) B-site cation ordering, (g)

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defect and domain wall motion, (h) annealing atmosphere and (i) phase transition

Effect of each one of these is as follows:

(a) **Concentration of secondary phases:** It has been a general observation that for prolonged annealing concentration of pyrochlore phases increases thereby reducing the dielectric constant, normally in lead based relaxor ferroelectrics [16].

(b) **Grain size:** In most of the articles in the literature, it has been found out that if no appreciable change in grain size takes place then no change in dielectric properties would be observed [16].

(c) **Density of ceramics after annealing:** If the density decreases during annealing, then it leads to reduction in the dielectric constant. Moreover, any change in density has to be judiciously correlated to the phases appearing after annealing. For instance, presence of certain heavy phases (like pyrochlore) may improve absolute density but reduce dielectric properties because of their inherently poor dielectric properties as observed in case of lead–zinc–niobate-based ferroelectric ceramics [16].

(d) **Composition of grain boundary layer:** If low dielectric constant phases like PbO rich phases are present along grain boundaries then dielectric constant is bound to decrease like in case of lead zinc niobate, lead magnesium niobate and lead iron niobate ferroelectric ceramics in as sintered condition. However, post-sinter annealing normally reduces the concentration of such grain boundary layers thereby improving the electrical properties [16,17]. Similar kind of observations have been made for spark plasma sintered antimony-doped tin oxide (ATO) ceramics wherein as sintered specimen contained amorphous regions at grain boundaries consisting of C, O, Si, Sn and Sb induced by surface segregation of Sb and contamination from graphite die during SPS and also during ball milling. However, after annealing amorphous region reduced in size. Moreover, C got removed due to annealing in air and oxygen vacancies were eliminated thus reducing the resistivity of ATO by two orders of magnitude to $5.68 \times 10^{-3}\ \Omega$ cm backed by the improvement in effective concentration of charge carriers and Hall mobility [4].

(e) **Release of internal stresses:** One of the main purposes of annealing is to reduce internal stresses thereby improving the domain wall motion and improving the dielectric properties. Release of internal stresses which resulted in easy domain wall, motion was helpful in improving the dielectric and ferroelectric properties of $Pb(In_{1/2}Nb_{1/2})O_3–xPbTiO_3$ ($x < 0.30$) ceramics which had been subjected to post-sinter annealing [16].

(f) **B-site cation ordering:** Annealing brings about B-site cation ordering by improving chemical homogeneity and improves dielectric properties. This phenomenon was responsible for improved microwave Dielectric Properties of $Ba(Co_{0.7}Zn_{0.3})_{1/3}Nb_{2/3}O_3$ Ceramics in which prolonged annealing at 1300 °C resulted in characteristic 1:2 cation ordering which resulted in significant improvement in quality factor wherein quality factor (Q_f) increased from 36,953 to 123,700 without appreciable change in grain size and dielectric constant [3].

(g) **Defect and domain wall motion:** Concentration of defects goes down after post-sinter annealing and thus, makes domain wall motion easy thereby improving dielectric and ferroelectric behavior. Moreover, significant improvement in dielectric constant takes place near to phase transition temperature where because of higher temperature, domain wall motion inherently becomes easy aided by declamping effect provided by removal of defects and internal stresses due to annealing as seen in lead zinc niobate based ferroelectric ceramics. However, it has to be also taken into consideration that prolonged annealing can also result in creation of vacancies of cations (especially Pb/Bi) and/or oxygen vacancies thereby increasing the dielectric constant along with increased electrical conductivity thereby limiting the usefulness of ceramic materials for dielectric application. Such kind of behavior has been observed in $(Pb_{0.75}Ba_{0.25})(Zr_{0.70}Ti_{0.30})O_3$, $BaBi_2Nb_2O_9$ ceramics [1,2].

(h) **Annealing atmosphere:** If the annealing is carried out in a sealed crucible then there is little chance for formation of cation (like Pb, Bi) or anion (oxygen) vacancies and thus, dielectric constant remain at low level. However, if the as sintered ceramic has huge concentration of cation/anion vacancies then annealing in sealed crucible would still produce high dielectric constant ceramics. However, such a high dielectric constant is accompanied by high electrical conductivity thereby limiting the dielectric applications of such materials. Therefore, sintering in oxygen rich or air atmosphere is necessary which reduces oxygen vacancy concentration significantly thereby improving the electrical resistivity of the ceramics [1,2]. Such kind of optimum combination of electrical resistivity and dielectric constant has been achieved in post-sinter annealed barium titanate ceramics which had exhibited colossal permittivity of about 3×10^5 in as microwave sintered condition because of large concentration of oxygen vacancies [18]. Reduction in dielectric constant and improvement in electrical resistivity has also been reported in $CaCu_3Ti_4O_{12}$ ceramics when post-sinter annealed in oxygen rich atmosphere. However, if such ceramics are annealed in argon or nitrogen, oxygen vacancy concentration cannot be brought down and thus, these ceramics continue to exhibit high dielectric constant and high electrical conductivity [19,20]. However, optimizing the annealing time is a key in this case because higher annealing time may result in the formation of cation vacancies or some undesired phase like pyrochlore which are detrimental from the application point of view.

(i) **Phase transition:** It has been observed in certain cases that post-sinter annealing induces, phase transition which can significantly improve ferroelectric and piezoelectric properties. In lead zinc niobate–lead titanate–barium titanate (PZN–PT–BT) ferroelectric ceramics, particles of BZN were present in an otherwise PZN–PT–BT matrix in as sintered condition. This resulted in presence of non-nano polar regions in a ferroelectric matrix which is Pb rich but BT lean. However, after annealing BZN particles were dissolved in matrix thus, bringing the composition closer to morphotropic phase boundary composition and significantly improved its dielectric and ferroelectric properties along with improvement in peak/maximum temperature T_m [21]. Similarly, Post-sinter annealing resulted in improvement of the piezoelectric

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