

Microhardness and dielectric properties of nanocrystalline magnesium phosphate

J. MATHEW*, S. KURIEN, K. C. GEORGE

Department of Physics, St. Berchmans' College, Changanacherry – 686 101, India

Nanocrystalline materials have attracted much attention due to their potential use as catalysts, sensors, ceramics and biomaterials. Materials with nanometer size have unusual electronic, magnetic, optical, and structural properties. Nanocrystalline magnesium phosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) of different grain sizes was prepared by changing the concentration of the reactants. The microhardness studies were carried out for different indentation loads for all the samples compacted under different pressures and their variations are plotted. Initially the hardness shows an increase with the load and then becomes practically independent of load. When the compacting pressure is gradually increased, the hardness also is seen to increase. The microhardness is further improved as the grain size of the sample is reduced. The dielectric properties of the prepared samples were analysed as a function of frequency and temperature. It is found that the dielectric constant (ϵ') and dielectric loss ($\tan \delta$) of all the samples decrease sharply as the frequency is increased and attains a constant low value at higher frequencies. The ac conductivity (σ_{ac}) has a low value at smaller frequencies, which increases as the frequency is increased. There is an upward shift in all these values as the temperature is raised and also when the grain size of the samples is reduced.

(Received March 5, 2007; accepted August 23, 2007)

Keywords: Nanocrystalline materials, Grain size, Microhardness, Dielectric properties

1. Introduction

Magnesium phosphate is an excellent chemically bonded phosphate ceramic (CBPC) binder used in refractories and mortars. They are an important ingredient in fertilizers and play a vital role in medical research. They are widely used in glass industry. Nanocrystalline magnesium phosphate ($\text{Mg}_2\text{P}_2\text{O}_7$) is selected for the present study, due to the fact that materials with nanometer size have unusual properties. The purification and size selection techniques developed produces nanocrystals with well-defined structure and morphology. The microhardness of a substance is an important parameter to define the strength of its material. This property is basically related to the crystal structure and the electronic factors operating to make the structure stable [1,2]. Among the various methods for hardness measurements, the micro indentation method using Vickers pyramid indenter is employed in this study. The strength of the nanophase microstructures is estimated from the Hall-Petch strengthening theory. The indentation load/size effect (ISE) on the microhardness has been considered on the basis of a variety of phenomena, including work hardening during indentation, the load to initiate plastic deformation, the activation energy for dislocation nucleation and plastic deformation band spacing. The enhanced electrical properties of nanocrystalline materials exhibiting unusual properties leads to the development of new materials [3,4]. The large surface to volume ratio of nanophase materials and the variations in electronic structure have dramatic effects on transport and catalytic properties. The effects of temperature and frequency on the dielectric behavior and

a.c. electrical conductivity offer valuable information about the conduction phenomenon in nanostructured materials. Dielectric behavior can effectively be used to study the electrical properties of grain boundaries, since majority of atoms in nanomaterials reside at grain boundaries [5-7].

2. Experimental

$\text{Mg}_2\text{P}_2\text{O}_7$ samples of different grain sizes are prepared by changing the molar concentration of the reactants to 1.0 molL^{-1} , 0.5 molL^{-1} and 0.1 molL^{-1} respectively. The micro hardness studies of the samples were carried out, using Leitz hardness tester type P 1191 fitted with a Vickers pyramidal diamond indenter [8]. The load P was varied from 0.1 N to 5 N, and the time of indentation was the same (30 sec.) for all trials and samples. For each sample, several trials of indentation with each load were made and the average values of the diagonal lengths of indentation marks were obtained. The Vickers microhardness number H_v was calculated using the relation

$$H_v = 1.8544 P/d^2 \quad (\text{GPa}) \quad (1)$$

where P is the applied load in N and d is the diagonal length of the indentation in m. In this study, the nanopowders of the samples obtained by chemical method, were collected and compacted for 2 minutes under pressures of 0.3 GPa, 0.34 GPa, 0.38 GPa and 0.41 GPa. The specimens were disc shaped, 13 mm in diameter and 1 to 2 mm in thickness. The density measurements of each specimen were performed based on Archimedes principle.

In order to study the dielectric behaviour, the nanoparticles were consolidated into pellets by applying a pressure of about 0.4 GPa. Both faces of the pellets were coated with colloidal silver. Conducting leads were attached to both faces of the pellets and the samples were then encapsulated using nonconducting epoxy powder. For electrical conductivity measurements, the encapsulated pellets were immersed in an oil bath, the temperature of which could be regulated with an accuracy of ± 0.1 °C. The capacitance (C_p), the modulus of complex impedance ($|Z|$) and phase angle (θ) of the samples were measured using a Hewlett-Packard 4192A impedance analyzer over the frequency range 100 Hz -3 MHz and over the temperature range 300 K to 373 K.

3. Results

Stoichiometric amounts of magnesium nitrate, aqueous solution of PVA (the matrix) and sucrose (the fuel) are mixed and evaporated to a viscous liquid. This fluffy, voluminous, carbonaceous mass is then thermolysed. The precursor powders are grounded and annealed at 900 °C for 4 hours to get the nanosized samples of different grain sizes [9].

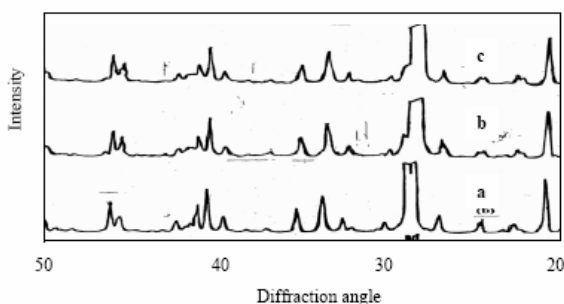


Fig. 1. XRD pattern of $\text{Mg}_2\text{P}_2\text{O}_7$ (a) 26 nm (b) 23 nm (c) 21 nm; all sintered at 900 °C, 4 hrs.

The XRD pattern of nano $\text{Mg}_2\text{P}_2\text{O}_7$ prepared with reactant concentration 1.0 mol L^{-1} , 0.5 mol L^{-1} and 0.1 mol L^{-1} (Fig. 1) shows that their grain sizes are 26 nm, 23 nm and 21 nm respectively. The crystal structures of all the samples are monoclinic.

The variation of microhardness with compacting pressures for the 26 nm $\text{Mg}_2\text{P}_2\text{O}_7$ sample is plotted in Fig. 2 (a). There is an increase of hardness up to a load of about 2 N and thereafter remain almost steady. Here H_v increases from about 900 GPa to 1100 GPa when the compacting pressure is increased from 0.3 GPa to 0.45 GPa. For the 21 nm sample, it is from about 900 GPa to 1200 GPa when the compacting pressure is increased as shown in Fig. 2 (b)

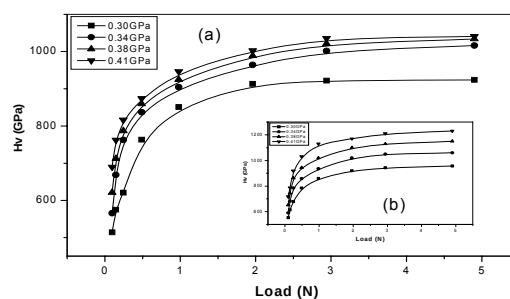


Fig. 2. Variation of microhardness with indentation loads of the $n\text{-Mg}_2\text{P}_2\text{O}_7$ samples.

Fig. 3(a) shows the variation of microhardness with densities for the 26 nm sample. The hardness increases from 0.6 GPa to 1.0 GPa for an increase in density from $1.675 \times 10^3 \text{ kg/m}^3$ to $1.75 \times 10^3 \text{ kg/m}^3$. For 21 nm sample shown in Fig. 3(b) the corresponding variation is from 0.675 GPa to 1.175 GPa.

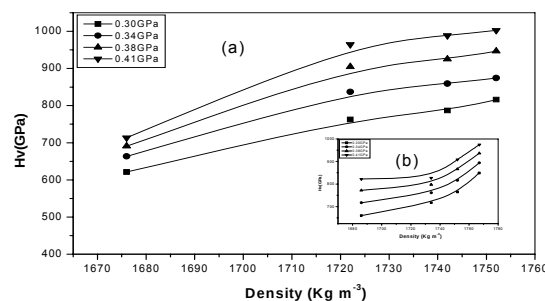


Fig. 3. Variation of microhardness with density of $\text{Mg}_2\text{P}_2\text{O}_7$ samples.

To examine the indentation load/size effect (ISE) on microhardness, it is necessary to evaluate an extensive set of measurements on the material to be studied. A plot of $\log P$ versus $\log d$ provides a straight line, the slope of which gives the work hardening coefficient n . These graphs, for the different samples studied, are plotted in Fig. 4. In the present study, work hardening coefficient n obtained using least square fit method is found to be less than 2 for all the samples. According to the Onsrich concept, [10] the lattice is soft if $n > 2$ and the lattice is hard if $n < 2$.

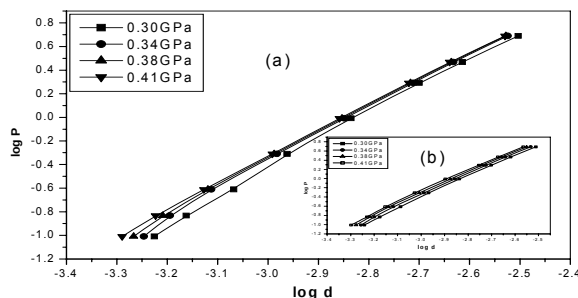


Fig. 4. $\log d$ vs $\log P$ graph for various compacting pressures of the $\text{Mg}_2\text{P}_2\text{O}_7$ samples.

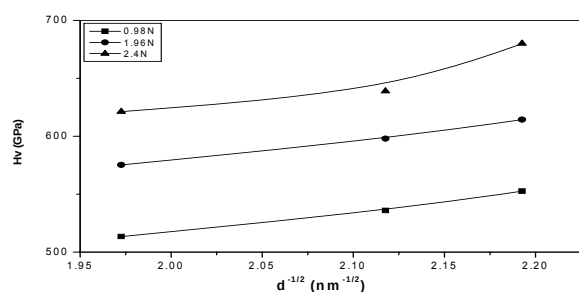


Fig. 5. Variation of microhardness with grain size of n - $\text{Mg}_2\text{P}_2\text{O}_7$ samples.

To investigate the effect of grain size on the hardness, [11,12] the values of the micro hardness number (H_v) are plotted with grain size ($d^{1/2}$) for all the samples as a function of indentation loads. It can be seen from the figures that the plots are more or less straight lines with positive slopes, showing that microhardness of each sample increases with decrease of grain size in accordance with the normal Hall-Petch relationship

$$H_v = H_0 + k d^{1/2} \quad (2)$$

The variation of microhardness of nanocrystalline magnesium phosphate of different grain sizes compacted under different pressures is given in Fig. 5. Here the value of H_v changes from 514 GPa to 553 GPa when the grain size changes from 26 nm to 21 nm for the compacting pressure 0.98 N. The change in H_v is from 621 GPa to 680 GPa, for the compacting pressure 2.4 N.

The dielectric constant ϵ' of the given samples were calculated from the measured values of capacitance C_p using the formula

$$\epsilon' = C_p d / \epsilon_0 A \quad (3)$$

where d is the thickness, A is the cross sectional area of the given sample, and ϵ_0 is the permittivity of free space. The variations of dielectric constant with frequency of the applied field of nano- $\text{Mg}_2\text{P}_2\text{O}_7$ samples for various temperatures are presented in Fig. 6 (a, b). At 300 K, the dielectric constant of 26 nm sample decreases from 105 at 100 Hz to 10 at 3 MHz. Similar variations are observed for other temperatures as seen from the figure. For 21 nm sample, the corresponding variation is from 648 to 14.

The variations of dielectric loss factor ($\tan\delta$) of nano $\text{Mg}_2\text{P}_2\text{O}_7$ samples with frequency are shown in Fig. 7 (a, b). The dielectric loss is given as

$$\tan \delta = \epsilon'' / \epsilon' = 4 \pi \sigma / \epsilon' \omega \quad (4)$$

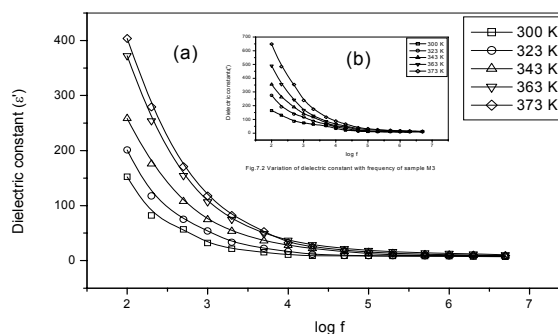


Fig. 6. Variation of dielectric constant with frequency at different temperatures.

where σ is the conductivity and ω is the frequency. It can be seen that $\tan \delta$ decreases with increase in frequency and at higher frequencies the loss angle has almost the same low value at all temperatures. For 26 nm sample, $\tan \delta$ at 373 K decreases from 2.5 to 0.25 as frequency increases from 100 Hz to 3 MHz. The corresponding variation for 21 nm sample is from 3.1 to 0.25. The same behaviour is observed with lower values for all other temperatures for both the samples.

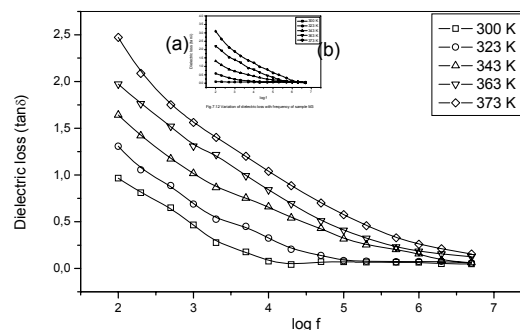


Fig. 7. Variation of dielectric loss with frequency of n - $\text{Mg}_2\text{P}_2\text{O}_7$ samples at different temperatures.

The variations of a.c. electrical conductivity (σ_{ac}) as a function of frequency and temperature for the samples are shown in Fig. 8(a, b). At low frequencies σ_{ac} is small, which increases as frequency increases. The nature is similar for other temperatures, but the values are increased as temperature increases. The peak value of σ_{ac} , in the present study, for 26 nm sample at 300 K is $0.875 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ while at 373 K, it is $1.9 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$. The corresponding variation for 21 nm sample is from $3.0 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ to $5.8 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$.

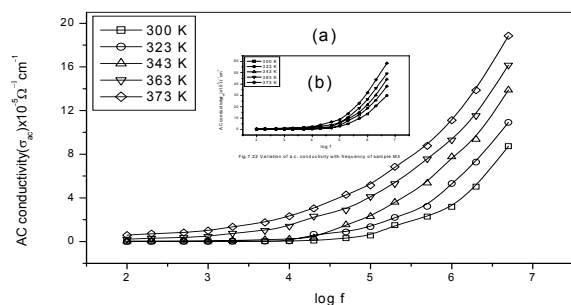


Fig. 8. Variation of a.c. conductivity with frequency at different temperatures.

The a.c. conductivity (σ_{ac}) of the samples is given by

$$\sigma_{ac} = 2\pi f \epsilon' \epsilon_0 \tan \delta \quad (5)$$

where f is the frequency, ϵ_0 is the permittivity of free space, ϵ' is the real part of the measured complex dielectric constant and $\tan \delta$ is the dielectric loss. The a.c. conductivities of all the samples depend strongly on the frequency of the applied field. The dispersion in conductivity of nanophase materials is due to the hopping of charge carriers around lattice imperfections [14]. An applied a.c. field will alter the energy difference between the traps in which electrons are confined and produces a net polarization, which is responsible for enhancing the a.c. conductivity.

4. Discussion

Due to the small size of grains and the large surface-to-volume ratio of nanocrystals, the atomic arrangements on the boundaries differ greatly from that of bulk crystals, showing some extent of disorder. This disorder in crystal symmetry leads to the broadening and shifting of many XRD bands in the crystal.

Significantly increased strength and ductilities have been predicted for nanophase microstructures. The strength of nanophase microstructures is estimated to be up to 30 times that of the coarse grain standard in some nanocrystals. Many authors [13,14] studied the micro hardness behavior of different nanostructured materials. Nieman, Weertman and Siegel [13] reported that nanocrystalline palladium samples (20 nm) show a four-fold increase in hardness compared to coarse-grained (100 μm) palladium and a doubling in hardness for nanocrystalline copper samples (25 nm) over coarse-grained (50 μm) copper. From the experimental results obtained in the present case, it can be seen that the microhardness of all the samples studied, is mainly affected by compacting pressure and change in grain size of the material. Thus the conclusion is that densification and reduction of grain size both together would increase the hardness of nanocrystalline samples.

Valuable information about various aspects has been brought out from the measurement of dielectric properties of nanostructured materials. Higher values of dielectric constant at low frequencies were reported for different materials by many authors [15-17]. As reported, the dielectric constant ϵ' of these ceramics depend very much on grain sizes. Most of the atoms in nanocrystalline materials reside on grain boundaries, [18] that become electrically active as a result of charge trapping. The large value of the dielectric constant of nanocrystalline materials at sufficiently high temperatures and at low frequencies is due to the combined effect of space charge polarization and conductivity effects, which increases the space charge concentration.

In nanophase materials, the grain boundaries have an amorphous or glassy structure [19]. All the inhomogeneities, defects, space charge formation etc. together produces an absorption current, which results in dielectric losses. Due to the presence of dangling bonds at the surface, the surface layers of nanoparticles will be highly reactive and there is a chance of adsorption of gases like oxygen or nitrogen. These adsorbed gases can also cause an increase in dielectric loss. Thus a nanophase material acts as a lossy dielectric with high dielectric loss at low frequencies, which decreases at higher frequencies.

The nature of frequency and temperature dependence of a.c. conductivity of the present samples, suggests an electronic hopping mechanism, exhibited by a large number of nanocrystalline materials. The physical significance of this type of frequency dependence comes from the fact that an alternating current can affect an electron confined to two traps [20,21]. The time it spends in each trap will depend on the energy difference of the two trap states. An applied a.c. field will alter this energy difference and produces a net polarization, which lags behind the field [21, 22]. This polarization, which is out of phase with the applied electric field, is measured as a.c. conductivity.

5. Conclusions

The variation of Vickers microhardness number (H_v) with indentation loads of all the studied specimens, shows an increase of hardness up to a load of about 2 N, and then remains practically constant, independent of load. The work hardening coefficient n was found to be less than 2, indicating that the sample is hard in nature. The micro hardness number (H_v) plotted with grain size ($d^{1/2}$) of all the samples are found to be straight lines with positive slopes, showing that microhardness of each sample increases with decrease of grain size in accordance with the normal Hall-Petch relationship. The dielectric constant and dielectric loss of all the samples are found to decrease with the applied frequency at all temperatures of measurement. The ac electrical conductivity (σ_{ac}) was found to increase with frequency for all samples. The dielectric constant, dielectric loss and ac conductivity depend strongly on grain size, frequency and temperature.

References

- [1] B. W. Mott, Butterworths Scientific Publication, London (1956).
- [2] M. A. Salim, G. D. Khattak, M. Sakhawatt Hussain, *J Noncrystalline Solids* **185**, 101 (1995).
- [3] J. Lee, J. H. Hwang, J. J. Mashek, T. O. Mason, A. E. Miller, R. W. Siegel, *J. Mater. Res.* **10**, 2295 (1995).
- [4] W. Puin, P. Heitjans, *Nanostructured Materials* **6**, 885 (1995).
- [5] Joshy Jose, M. Abdul Khadar, *Nanostructured Materials*. **2**(8), 1091 (1999).
- [6] W. D. Kingery, "Introduction to Ceramics", John Wiley, New York, 2nd Ed. (1976).
- [7] C. Mo, Z. Yuan, L. Zhang, C. Xie, *Nanostructured Materials* **2**, 47 (1993).
- [8] G. E. Fougere, J. R. Weertman, R. W. Siegel, S. Kim, *scripta Met. et Mater.* **26**(12), 1879 (1992).
- [9] P. Pramanik, *Bull. Mater. Sci.* **22**(3), 335 (1999).
- [10] E. M. Onitsch, *Mikroskopie*. **95**, 12 (1950).
- [11] Valerie Montouillout, Dominique Marsiot, Andre Douy, Jean Pierre Coutures, *J. Amer. Ceram. Soc.* **82**, 12 (1999).
- [12] F. M. Ernsberger, *J. Am. Ceram. Soc.* **51**, 545 (1968).
- [13] C. W. Nieman, J. R. Weertman, R. W. Siegel, *Scripta Met. et Mater.* **23**(12), 2013 (1989).
- [14] Yuchui Xiao, R. James Kirkpatrick, *J. Mater. Res.* **10**, 10 (1995).
- [15] R. W. Siegel, "Physics of New Materials", Ed. F E Fujita (Springer- Verlag, New York, 1994) p. 65.
- [16] H. Gleiter, *Nanostructured Materials* **6**, 3 (1987).
- [17] Makato Aoki, Yet-Ming Chiang, Igor Kosacki, L. Jong-Ren Lee, Hurry Tuller, Yaging Liu, *J. Am. Ceram. Soc.* **79**, 1169, (1996).
- [18] V. Biju, M. A. Khadar, *J. Mater. Sci.*, **38**, 4055 (2003).
- [19] R. W. Seigel, *Phys. Today*: **64** October (1993).
- [20] F. Argall, A. K. Jonscher, *Thin solid Films* **2**, 185 (1968).
- [21] A. K. Jonscher, *J. Non-Cryst. Solids* **8-10**, 293 (1972).

*Corresponding author: profjos@gmail.com