High-pressure high-temperature transitions in nanocrystalline γ Al_2O_3 , γ Fe_2O_3 and TiO_2

S N VAIDYA

Condensed Matter Physics Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

Abstract. We report first observation of new polymorphs of Al_2O_3 and Fe_2O_3 in specimens of xerogel γ Al_2O_3 and γ Fe_2O_3 quenched from high pressures and temperatures. At about 5 GPa and 1400°C, xerogel gamma alumina (XGA) transformed into a polymorphic mixture of phases α Al_2O_3 , B Al_2O_3 and C Al_2O_3 , while XGA containing 1 wt% Cr_2O_3 transformed into a mixture of phases α Al_2O_3 , H Al_2O_3 and k' Al_2O_3 . The phases B Al_2O_3 , C Al_2O_3 and H Al_2O_3 have the monoclinic-, cubic- and hexagonal-rare earth sesquioxide (Ln_2O_3) type structure, respectively. At 5.2 GPa and 1450°C, XGA yielded a mixture of α Al_2O_3 and hexagonal μ Al_2O_3 . At STP, the phase μ Al_2O_3 was found to transform to another hexagonal phase λ Al_2O_3 over a 10 week period.

At 5.2 GPa and 900°C, γ Fe_2O_3 showed transition to a new phase H Fe_2O_3 which probably has an 8 layer close packed structure. In nanocrystalline TiO_2 , only the anatase to rutile transition was found. The results are discussed using the free energy vs temperature diagram for xerogel and nanocrystalline materials.

Keywords. Al_2O_3 ; Fe_2O_3 ; nanocrystalline phase; high pressure/temperature.

1. Introduction

The experimental studies have shown that the physical and chemical properties of materials change substantially from their bulk values when the crystal dimension is reduced. For small particle size, some nanocrystalline (n) solids occur as polymorphs which have lower density and different structure from that of the bulk material. Thus nanocrystalline alumina for average crystallite size < 200 Å occurs as cubic γ alumina ($\rho = 2.71$ g/cc⁻¹), for crystallite size in range 250–400 Å as monoclinic θ alumina and for crystallite size > 400 Å as rhombohedral α alumina ($\rho = 3.99$ g/cc⁻¹) (Ayyub *et al* 1995). Many other systems such as Fe_2O_3 , Y_2O_3 , Mn_2O_3 , ZrO_2 , ZnS and CdS also show phase change as the particle size is reduced (Ayyub *et al* 1988; Khosravi *et al* 1995; Kundu *et al* 1997). Nanocrystalline materials show pronounced chemical activity due to their large surface area. A number of industrial catalysts are derived from nanocrystalline forms of alumina, silica and titania containing, at times, transition group or platinum group metals and alloys.

The principal methods used for preparation of nanocrystalline solids are the solution sol gel method, high temperature self combustion synthesis and condensation of vapours on cold substrates in helium or argon atmosphere (Suryanarayana 1995; Mayo 1996). In the sol gel method, an ultrahomogeneous mixture prepared by dissolving appropriate metal salts in water is converted into gel by using appropriate molarity, pH, temperature and gelation time (Roy 1987). The gel is desiccated and sintered, in most cases, around 500°C to yield highly

dispersed xerogels which are often a mixture of nanocrystalline and amorphous phases. In the self combustion synthesis, the gel produced from redox solutions is heated to ignition. The heat of combustion fragments material into fine particles (Aruna and Patil 1996; Porkin 1996). Production of fine particles by thermal decomposition of metal hydroxides, hydrated oxides, carbonates, oxalates, citrates etc is also in this category. Synthesis of nanocrystalline diamond by detonation of carbon containing explosives is another example of stabilization of a low density phase by the fragmentation technique (Mayo 1996). The vapour condensation technique mostly yields nanocrystalline metals or metal oxides (Birringer *et al* 1984). The transmission electron microscopic studies are used for characterization of phases, determination of grain size and pore size distribution in nanocrystalline materials.

Nanocrystalline solids which occur as polymorphs of low density can be expected to transform to a dense polymorphic form at high pressures and temperatures. In this paper we present the results of high-pressure high-temperature studies on n γ Al_2O_3 , n γ Fe_2O_3 and n TiO_2 which led to the first observation of new polymorphic forms of Al_2O_3 and Fe_2O_3 (Vaidya *et al* 1998a, b). High pressure studies on nanocrystalline CdS and CdSe (Chen *et al* 1997) and on xerogel silica (Dubrovinski *et al* 1997) have been reported recently.

2. Experimental

The high purity xerogel alumina was prepared by sol gel method using aluminum isopropoxide. The dried material was powdered and heated to 500°C for 15 h to

obtain the xerogel (Yoldas 1975). $n\text{Fe}_2\text{O}_3$ was prepared from hydrated iron nitrate and matonic acid dihydrazide, and $n\text{TiO}_2$ (A) was prepared from $\text{TiO}(\text{NO}_3)_2$ and oxalyl dihydrazide, by self combustion synthesis (Aruna and Patil 1996). $n\text{TiO}_2$ (R) was prepared by the sol gel method. The materials were characterized by XRD and the size of the coherently diffracting region was obtained by using Scherrer formula

$$\alpha = 0.9\lambda/B \cdot \cos \theta,$$

where B is the full width at half maximum and θ gives the peak position of the diffraction line.

High-pressure high-temperature experiments were carried out in internally heated toroid apparatus fitted with anvils of 32 mm face diameter (Karunakaran and Vaidya 1997). The material was compacted in BN containers. It was subjected to required pressure and temperature for 15 min and quenched by cutting off the power. The XRD patterns of the recovered materials were recorded with CuK_α radiation using PW 1820 wide angle goniometer.

3. Results

3.1 $n\gamma\text{Al}_2\text{O}_3$

It is seen from figure 1 that xerogel γ alumina (XGA) as well as xerogel γ alumina containing 1 wt% Cr_2O_3 (XGAC) is a mixture of nanocrystalline $\gamma\text{Al}_2\text{O}_3$ and an amorphous phase. We found using Bridgman anvils that at 27°C XGAC becomes completely amorphous at about 5 GPa.

The XRD pattern of the XGA quenched from 5.2 GPa and 1450°C is shown in figure 2. The product was found to be a mixture of $\alpha\text{Al}_2\text{O}_3$, monoclinic BAl_2O_3 ($a = 14.526$, $b = 3.560$, $c = 8.446$ Å and $\beta = 99.49^\circ$) which is isomorphous with BSm_2O_3 (S.G. C 2/m), and cubic CAl_2O_3 ($a = 10.999$ Å) which is isomorphous with CSm_2O_3 (S.G. Ia3). The coordination member of aluminum which is 6 in Al_2O_3 increases to 7 in the rare earth sesquioxide structures. The XRD pattern XGAC quenched from 5.2 GPa and 1450°C is shown in figure 3. The product was found to be a mixture of $\alpha\text{Al}_2\text{O}_3$, hexagonal HAl_2O_3 ($a = 3.844$ and $c = 6.103$ Å) which is isomorphous with HSm_2O_3 , and an intermediate phase $\text{k}'\text{Al}_2\text{O}_3$ (S.G. $\text{P6}_3\text{mc}$; $a = 5.494$ and $c = 8.574$ Å). Thus under these conditions $\gamma\text{Al}_2\text{O}_3$ is converted into polymorphs which are isomorphous with the high temperature polymorphs of Y_2O_3 , Gd_2O_3 and Sm_2O_3 (Landolt and Bornstein 1975).

The XGA and XGAC however showed transition to a metastable phase $\mu\text{Al}_2\text{O}_3$ at somewhat lower pressures and temperatures. The XRD pattern of the XGAC quenched from 4.56 GPa and 1100°C taken soon after

the experiment (figure 4) showed that the material is a mixture of $\alpha\text{Al}_2\text{O}_3$ and a new hexagonal phase $\mu\text{Al}_2\text{O}_3$ with $a = 5.8766$ and $c = 17.757$ Å. At STP, $\mu\text{Al}_2\text{O}_3$ transformed in about 10 weeks to another hexagonal phase $\lambda\text{Al}_2\text{O}_3$ (figure 5) with $a = 9.8285$ and $c = 18.100$ Å. However, the positions of the $\alpha\text{Al}_2\text{O}_3$ diffraction lines did not show any change. It is seen that $a_\lambda = \sqrt{3}a_\mu$ and $c_\lambda = c_\mu$. The phase μ - and λ -alumina are probably superstructures of the phases k' alumina (hex. $a = 5.544$ and $c = 9.024$ Å) and k'' alumina (hex. $a = 9.599$ and $c = 9.015$ Å), respectively which are formed during the dehydration of tohedite $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (Okumiyama *et al* 1971). The XGA quenched from 5.2 GPa and 1400°C also showed formation of μ - and λ -alumina. Complete conversion to $\alpha\text{Al}_2\text{O}_3$ was found to occur in XGAC at 5.2 GPa and 1520°C (figure 6).

Figure 1. XRD pattern of (a) xerogel alumina (XGA), (b) XGA containing 1 wt% Cr_2O_3 (XGAC) and (c) XGAC pressurized to 8 GPa.

Figure 2. XRD pattern of XGA quenched from 5.2 GPa and 1400°C.

Figure 3. XRD pattern of XGAC quenched from 5.2 GPa and 1450°C.

3.2 $n\gamma\text{Fe}_2\text{O}_3$

The XRD pattern of $n\text{Fe}_2\text{O}_3$ confirmed the phase with cubic maghemite C structure ($\rho = 8.344 \text{ \AA}$). The background due to the amorphous phase was rather small.

The average particle size was $\sim 200 \text{ \AA}$ and the BET area $45 \text{ m}^2\text{g}^{-1}$. $\gamma\text{Fe}_2\text{O}_3$, like $\gamma\text{Al}_2\text{O}_3$, showed transition to amorphous phase at about 8 GPa at 27°C . The material quenched from 5.2 GPa and 650°C showed that it retains maghemite C structure but the diffraction lines were

Figure 4. XRD pattern of XGAC quenched from 4-56 GPa and 1100°C soon after the experiment.

Figure 5. XRD pattern of XGAC quenched from 4-56 GPa and 1100°C 10 weeks after the experiment.

Figure 6. XRD pattern of XGAC quenched from 5.2 GPa and 1520°C.

sharp due to increase in the crystallite size. The material quenched from 5.2 GPa and 900°C showed a new phase HFe_2O_3 in addition to maghemite C (figure 7). The lines were indexed on hexagonal cell with $a = 10.745$, $c = 17.882$ Å and $c/a = 1.66$. This suggests an 8-layer ($c = 8 \times 2.23$ Å) close packed structure in which Fe atoms occupy octahedral or tetrahedral sites. In keeping with the hexagonal symmetry, the sequence of layers can be either ...*hhhchhhc*... or ...*ccchccch*... (Wells 1962). The alloy $\text{Fe}_{2.5}\text{V}_6\text{O}_{16}$ crystallizes in space $\text{P6}_3\text{mc}$ with $a_x = 5.874$ and $c_x = 9.295$ Å and has a close packed structure in which Fe and V atoms occupy some tetrahedral and some octahedral voids (Wycoff 1966).

3.3 $n\text{TiO}_2$

The $n\text{TiO}_2$ (A) employed had average particle size of 94 Å and BET area $90\text{ m}^2\text{g}^{-1}$ and the particle size of $n\text{TiO}_2$ (R) was 90 Å. $n\text{TiO}_2$ (A) showed onset of transition to amorphous phase at about 6 GPa at 27°C. Anatase to rutile transition was found to be $n\text{TiO}_2$ (A) quenched from 5.2 GPa and 700°C. No other phase changes were found in this system in the pressure and temperature investigated.

4. Free energy diagram of xerogel

The free energy vs temperature diagram, proposed by Roy (1969) and Hoffman *et al* (1984) for various phases

Figure 7. XRD pattern of $n\gamma\text{Fe}_2\text{O}_3$ quenched from 5.2 GPa and 900°C.

is shown in figure 8. The xerogel has very high free energy because of large surface area of crystallites and presence of defects and amorphous phase. The diagram assigns still higher free energy to diphasic xerogel such as XGAC. The amorphous phase is more compact and has a lower free energy and the nanocrystalline phase which is more ordered has still lower free energy. The

Figure 8. Schematic variation of free energy with temperature.

metastable phases are next in the order of decreasing free energy. The diagram depicts curve for liquid, the melting point T_m and defines transition temperatures T_g , T_n and T_{ms} .

The free energy diagram suggests that for $T < T_g$, xerogel can transform to any phase having lower free energy, including the amorphous phase. The pressure induced transition of xerogel $\gamma\text{Al}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$ and $n\text{TiO}_2$ (A) to amorphous phase at 27°C is in accordance with arrow marked 1 in this diagram. For $T_g < T < T_m$, the xerogel can transform to a mixture of metastable and crystalline phases. The phase transitions observed in XGA, XGAC and $n\gamma\text{Fe}_2\text{O}_3$ at high pressures and temperatures are in accord with this scheme and are represented by arrow 2 in the diagram. The anatase to rutile transformation in $n\text{TiO}_2$ (A) at high pressures and temperatures proceeds without formation of intermediate phases because no metastable phases other than anatase and brookite are found in this system. Finally, the complete conversion of XGAC to $\alpha\text{Al}_2\text{O}_3$ is in accordance with the scheme depicted by arrow 4 for $T_{ms} < T < T_m$.

5. Dehydration of hydrated oxides and hydroxides

The minerals gibbsite $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, tohdite $5\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, boehmite $\alpha\text{AlO}(\text{OH})$ and diaspor $\beta\text{AlO}(\text{OH})$ on heating first transform to intermediate structures and finally to $\alpha\text{Al}_2\text{O}_3$ above 1200°C (Landolt and Bornstein 1975). The sequence of dehydration products of gibbsite depends on whether it is heated in moisture or vacuum (Structure Reports 1960, 1961). In presence of moisture it shows sequence of phases

while in air it shows the sequence

Except $\alpha\text{Al}_2\text{O}_3$ which is cubic, and $\theta\text{Al}_2\text{O}_3$ which is monoclinic, all other intermediate phases are hexagonal. In fact, $\phi\text{Al}_2\text{O}_3$ represents a group of hexagonal structures reported by Brindley and Choe (1961). The transformation in $\theta\text{Al}_2\text{O}_3$ and boehmite are given in this sequence. The mineral tohdite transforms to hexagonal $k'\text{Al}_2\text{O}_3$ around 750°C and to $k''\text{Al}_2\text{O}_3$ at higher temperatures. Diaspor exhibits between 300 and 1000°C transformation to a monoclinic phase $\alpha'\text{Al}_2\text{O}_3$ which is closely related to $\alpha\text{Al}_2\text{O}_3$ (Carim *et al* 1997).

Controlled dehydration of iron hydroxide also gives intermediate structures. A large number of polymorphs maghemite C, $\beta\text{Fe}_2\text{O}_3$, $\gamma\text{Fe}_2\text{O}_3$, $\epsilon\text{Fe}_2\text{O}_3$ etc have been identified (Landolt and Bornstein 1975). TiO_2 has only two metastable phases anatase and brookite.

The formation of very fine powders of intermediate structures on dehydration of hydrated oxides or hydroxides is associated with expulsion of water and fragmentation of lattice. However, due to aggregation of particles, the particle size cannot be controlled in this process. The results of our experiments suggest that in the systems which exhibit richness of intermediate structures, the nanocrystalline materials can transform to intermediate (or metastable) crystalline phases at high pressures and temperatures.

6. Conclusions

The present study has shown that in a certain range of pressures and temperatures, nanocrystalline solids transform to a polymorphic mixture. The metastable phases are more likely to be formed in oxides if the corresponding hydroxides or hydrated oxides show a richness of intermediate phases at high temperatures. The intermediate phases are formed only over a limited range of pressures and temperatures and stable phase is formed if $T > T_{ms}$ (P). In XGAC, for instance, no intermediate phases are formed above 5.2 GPa and 1520°C. It follows from figure 8 that above T_{ms} (P), the nanocrystalline and metastable phases all transform to stable crystalline phase. Hence above certain pressure and temperature, the nanocrystalline and stable crystalline solid will show same phase transition behaviour. This contention is supported by laser heated DAC experiments on sol gel silica and quartz. Both were found to transform to a new structure, which is intermediate between αPbO_2 and

ZrO_2 structure, at pressures 62–85 GPa and temperatures > 2000 K (Dubrovinsky *et al* 1997).

The presence of residual water and impurities can have profound effect on phase transitions in xerogels and nanocrystalline materials. These effects have been extensively studied in mineral synthesis at high pressures and temperatures, and similar work is needed on xerogels also.

The xerogels and nanocrystalline solids show rather low crystallization temperature which implies that the activation energy of crystallization is quite small. Easy sinterability forms the basis of their widespread application in ceramic industry (Roy 1987). The low activation energy of the xerogels and nanocrystalline solids reduces the pressure and temperature of transformation. Thus cubic BN is readily synthesized in presence of Li_3N at high pressures and temperatures from turbotactic BN which is probably a nanocrystalline material. Similarly, nanocrystalline form of carbon, fullerene, can be converted to diamond by application of pressure alone while the conversion of graphite to diamond requires both high pressures and temperatures.

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References

- Aruna S T and Patil K C 1996 *J. Mater. Syn. Process.* **4** 175
 Ayyub P, Multani M, Burma M, Palkar V R and Vijayaraghavan R 1988 *J. Phys.* **C21** 2229
 Ayyub P, Palkar V R, Chattopadhyaya S and Multani M 1995 *Phys. Rev.* **B51** 6135
 Birringer R, Gleiter H, Klein H P and Marquardt P 1984 *Phys. Lett.* **A102** 365
 Brindley G W and Choe J O 1961 *Am. Min.* **46** 771
 Carim A H, Rohrer G S, Dando N R, Tzeng S Y, Rohrer C L and Perotta A J 1997 *J. Am. Ceram. Soc.* **80** 2877
 Chen C, Herzhold A B, Johnson C S and Alivosatos A P 1997 *Science* **276** 398
 Dubrovinsky L S, Saxena S K, Lazor P, Ahuja R, Eriksson O, Willis J M and Johansson B 1997 *Nature* **388** 362
 Hoffman D W, Roy R and Komarneni S 1984 *J. Am. Ceram. Soc.* **67** 468
 Karunakaran C and Vaidya S N 1997 *High Temp. High Press.* **26** 393
 Khosravi A A, Kundu M, Kuruvilla B A, Shekhawat G S, Gupta R P, Sharma A K, Vyas P D and Kulkarni G K 1995 *Appl. Phys. Lett.* **67** 2506
 Kundu M, Khosravi A A, Kulkarni S K and Singh P 1997 *J. Mater. Sci.* **32** 245
 Landolt and Bornstein 1975 *Crystal structure data of inorganic compounds* (Berlin: Springer) New series. vol. III/b7
 Mayo M J 1996 *Int. Metals Rev.* **41** 85
 Oumiya M, Yamaguchi G, Yamada O and Ono S 1971 *Bull. Chem. Soc. Jap.* **44** 418
 Porkin I P 1996 *Chem. Soc. Rev.* 199
 Roy R 1969 *J. Am. Ceram. Soc.* **52** 344
 Roy R 1987 *Nature* **238** 1664
 Structure Reports 1960 **24** 307; 1961 **26** 347
 Suryanarayana C 1995 *Int. Metals Rev.* **40** 41
 Vaidya S N, Karunakaran C, Kamath R V, Pillai K T and Vaidya S N 1998a *High Press. Res.* (in press)
 Vaidya S N, Karunakaran C, Aruna S T, Achary S N and Tyagi A K 1998b (in preparation)
 Wells A F 1962 *Structural inorganic chemistry* (London: Oxford University Press) 3rd Ed. pp. **116** 489
 Wyckoff R W G 1966 *Crystal structures* (New York: Interscience) 2nd ed., Vol. 4, p **38**
 Yoldas B E 1975 *Am. Ceram. Soc. Bull.* **54** 285