Influence of Anatase and Rutile Phases on Physical Properties of new Nanosize $MgTi_2O_5$

A.H.KARANDE[1], S.Y.SHINGARE[2], S.S.GURAV[3], S.V. SALVI[4]

1. Department of Physics, Maharshi Dayanand College,Parel, Mumbai – 400012, India.
2. Department of Physics, Institute of Science, 15, Madam Cama Road, Mumbai – 400 032, India.
e-mail: ahk1712@gmail.com

Abstract

$MgTi_2O_5$ (A) and $MgTi_2O_5$ (R) are synthesized by the high temperature solid state reaction techniques using MgO and anatase TiO_2 (A) and rutile TiO_2 (R) respectively. The lattice parameters, porosity, inhomogeneity, and particle size are found to be larger in sample R by XRD technique. The empirical model proposed to determine the degree of disorder found to be larger for sample R which may be attributed to faster reaction mechanism in it.

Key words : karrooite($MgTi_2O_5$), rutile, anatase, disorder

Introduction

$MgTi_2O_5$ occurs as a natural mineral. It received much attention during the Apolo mission because of their implications in the cooling histories of lunar basalts. Also it exhibits an unusually large thermal anisotropy. It is an important constituent of refractory ceramics and magnetic materials [1].This ceramic has high permittivity, high Q, good thermal stability. Various methods have been used to synthesize $MgTi_2O_5$. A wide range of non-convergent cation order – disorder between two crystallographically distinct octahedral sites (M1 and M2) in $MgTi_2O_5$ is responsible for its high temperature stabilization. In most of the reports the phase of TiO_2 has not been mentioned, the fact that the anatase phase gets converted to the rutile phase at as low as 400°C and that most of the reaction occurs at temperatures much higher than 400°C. Whereas some transition metal oxides have accelerating power on anatase – rutile transformation. The, temperature and time of anatase to rutile transformation varies which strongly depends on many factors such as presence of impurities, deviation of stoichiometry, surface area, particle size, and atmosphere. Therefore it is thought worthwhile to synthesize $MgTi_2O_5$ using both the rutile and anatase and investigate the influence of the phases on physical properties of $MgTi_2O_5$.

Experimental

$MgTi_2O_5$ is prepared by calcining a homogenized and stoichiometric mixture of fine powder of AR grade MgO and TiO_2 (anatase) for sample (A) and TiO_2 (rutile) for sample (R) at 1000°C for 120 hours. Finally sintering of both the samples is carried out at 1200°C for 24 hours. A microprocessor based

JEOL JDX – 8030 X – Ray diffractometer is used to determine the XRD data of the sample. 'PERKIN – ELMER 683' spectrophotometer is used to determine IR spectra.

Result and Discussion

Structural properties: XRD data of both the samples are indexed in orthorhombic structure. The relative percentage intensities of most prominent atomic planes with their Miller indices of both samples. In both samples (101) plane show highest relative percentage intensity. The intensity of (230) plane in sample A is relatively larger and the intensities of other planes are relatively smaller than corresponding to sample R.

The lattice parameters are observed to be smaller in sample R than A as in Table 1. It results in smaller unit cell volume. It is observed that sample A has more pore fraction than R which may be the reflection of vertex sharing of TiO_2 (anatase). Debye particle size is larger for sample R perhaps due to strain free growth of lattice which is indicated by smaller inhomogeneity as in fig.1.

Table 1: Lattice parameters, pore fraction, inhomogeneity & average particle size of the $MgTi_2O_5$ samples A and R.

Sample	A (°A)	b (°A)	C (°A)	Particle size (nm)	Pore fraction	Inhomogeneity
A	9.7432	10.0095	3.7441	55	0.268	0.107
R	9.7160	9.9652	3.7365	67.1	0.050	- 0.004

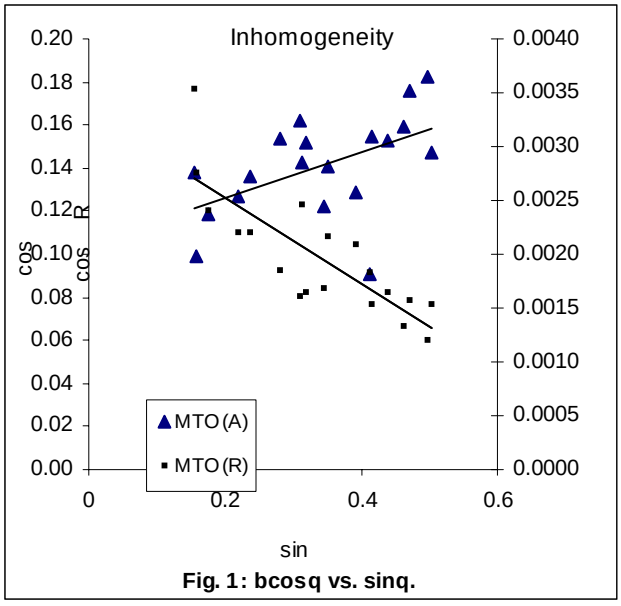

Fig. 1: bcosq vs. sinq.

Thermodynamic properties

The karrooite exhibits different cation distribution in the M1 and M2 sites depending on the heat treatment. The cation distribution is well described by the degree of disorder [2] and the order parameter [3]. The knowledge of degree of disorder is necessary to determine enthalpy, entropy and Gibbs free energy. The degree of disorder is correlated strongly with lattice parameters. Therefore, in the present paper, we have developed an empirical model based on lattice parameters 'a', 'b' and 'c' to determine the degree of disorder. It is well calibrated with the reported disorder (x) data [4]. Using this formula as a standard one, the degree of disorder corresponding to $MgTi_2O_5$ samples A and R is determined.

$$X = 586.241\ (c/b) - 188.154\ (c/a) - 150.822\ (a/b)$$

The degree of disorder (x) determined from the above model is smaller for sample A than for R. The enthalpy, configurationally entropy and Gibbs free energy are functions of degree of disorder are reported in Table 2. The enthalpy of sample A is greater than double that of sample R which clearly indicates that more heat is required for karrooite phase formation. Hence the reaction mechanism is faster in sample R.

Table 2 : Thermodynamic parameters of $MgTi_2O_5$

Sample	Enthalpy (J/mol.) x 10^3	Config. Entropy (J.mol^{-1} K^{-1})	Gibbs free energy (J)	Order (s)	Degree of disorder (x)
A	48.026	8.724	35175	0.654	0.173
R	21.502	13.992	892	0.190	0.405

IR Spectra

IR spectra for both samples are reproduced frequencies of absorption band which are around 640 cm^{-1} and 500 cm^{-1} are assigned to octahedral stretching modes corresponding to M1 and M2 sites respectively.

Table 3 : IR bands of $MgTi_2O_5$ samples A and R.

IR bands	A	R	Possible bond assignment	Site
ν_1 (cm^{-1})	641.2	648.0	Mg – Ti stretching	M1 octahedral
ν_2 (cm^{-1})	509.8	505.3	Mg – Ti stretching	M2 octahedral

It is observed from Table 3 that the separation in bands increases with degree of disorder. This means the stronger correlation between M1 and M2 sites prevails when the content of Ti increases on the M2 site.

Conclusion

The reaction mechanism is faster in sample R than sample A due to the grater degree of disorder.

References

1. H. Yang, R. M. Hazen, J. Solid State Chem., 138, 238 (1998).
2. B. A. Wechsler, A. Navrotsky, J. Solid State Chem., 55, 165 (1984).
3. M. S. Ghiorso, H. Yang, R. M. Haxen, Am. Miner., 84, 1370 (1999).
4. R. A. Nyquist, " Infrared spectra of Inorganic compounds" NY, (1971).