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Study of curious spiral like features in inverse spinel compound (Mg_2TiO_4)

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ABSTRACT

Qandilite (Mg_2TiO_4) pellets have been made by conventional solid state reaction technique on sintering at 1300 ºC. The main focus of this paper is on the morphological investigation of the inverse spinel (Mg_2TiO_4). The surface morphology of the sample (Mg_2TiO_4) is investigated by Scanning Electron Microscopy (SEM) which shows the occurrence of curious cubical growth characteristics resembling a spiral like features which have emanated from screw dislocations.

Introduction:

The term spinel is derived from spina (Latin, thorn) in reference to its pointed octahedral crystal habit. Spinel compounds / Oxides are the group of minerals that are oxides of Magnesium, Iron, Manganese or Aluminum etc. The general chemical composition is AB_2O_4. A and B can be divalent (with radii between 80 and 110 pm), trivalent (with radii between 75 and 90 pm) or quadrivalent cations, including Magnesium, Zinc, Iron, Manganese, Aluminum, Chromium, Titanium, Silicon and Cobalt with the general formulation $A^{2+}B_2^{3+}O_4^{2}$. A and B occupy some or all the octahedral and tetrahedral sites in the crystal lattice. Spinel oxides are the richest families having a number of compounds and diversity of observed physical properties such as ferromagnetic ordering, metal insulator transition, heavy fermion behavior, charge ordering and superconductivity [1-9]. Spinels are widely employed to deduce the evolutionary history of rocks because the compositions are extremely sensitive to environmental conditions of formation. Spinels also occur as semi-precious gems and are widely employed as mechanically robust ceramics. The minerals are strongly magnetic in nature, similar to magnetite. They are soluble in hot HCl, but only partially soluble in cold HCl, hot H_2SO_4 and HNO_3.

The ideal spinel formula is $MgAl_2O_4$ which refers to spinel type structure (Space group Fd3m and Z=8). Its formula is $(Mg)^{2+}[Al^{3+}]O_4$. The round and square brackets denote tetrahedral and octahedral sites respectively, while the oxygen ions are arranged in a cubic closed packed structure. The essential elements of spinels are Al, Mg and O with Ti, Fe, Zn, Mn and Ca as the most common impurities [10].

The compound Mg_2TiO_4 refers to the inverse (reversible) spinel type structure (Space group Fd3m and Z=8) with structural formula $(Mg)^{2+}[Mg^{2+}Ti^{4+}]O_4$ [11]. In this compound, half of the magnesium ions arrange themselves on tetrahedral sites and the other half, together with titanium, occupy octahedral positions. Mg_2TiO_4 can also be used as novel substrate for epitaxial growth of high temperature superconducting thin films [12]. It is also used as a heat resistor [13], dielectric for microwave technology, capacitor for temperature compensation and refractory material [14]. In the present work, inverse spinels Mg_2TiO_4 is investigated for its morphological characteristics.

Growth mechanism:

Each crystal system tends to display a unique defect structure; such defects are introduced during the crystal growth stage. The application of any crystal relies solely upon the functionality of these materials for which it is crucial to control the defects and the crystal size [15]. The growth mechanism in case of spinel structures is detrimental as a minor change in the occupancy of tetrahedral or octahedral sites results in either a spinel type or inverse spinel type structure. The resulting pattern is a curious spiral like structure; each grain or column grows by adding atoms to a spirally expanding ramp on the top surface of the grain [16] as proposed by Frank [17] in the classical spiral growth mechanism. These dislocations will create steps in the surface, obviating the necessity for 2D nucleation. Fig. 1 shows a schematic diagram on the formation and development of spiral growth. The spiral growth mechanism was developed theoretically by Buston et. al. [18] and observed experimentally for the first time by Verma & Krishna [19]. The theory of crystal growth by spiral dislocation was further refined by Buston, Cabrera and Frank [18] giving rise to what is known as BCF theory.

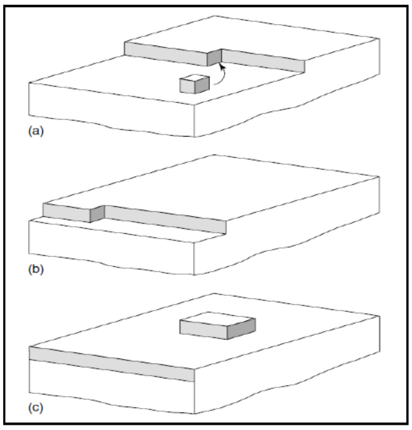

Fig: 1. Schematic representation of layer growth (a) Incorporation of growth units into step; (b) step has almost advanced to the edge of the crystal; (c) formation of 2D nucleus.

Materials and method:

Polycrystalline sample of inverse spinel Mg_2TiO_4 was synthesized by solid state reaction technique, with composition $Mg_{2-x}Ti_{1-x}O_4$, where x is called the inversion parameter. The stoichiometric amount of $Mg(NO_3)_2.6H_2O$ (98.5 %) and TiO_2 (Rutile, 99.5 %), powders were mixed thoroughly and pre calcined for 12 h at 1000º C. The pre calcined material was again ground and calcinated at 1250 ºC for 24 h. Finally the sample was ground to fine powder, pressed to pellet form and sintered at 1300 ºC for 72 h and at the end of heat treatment the sample was allowed to cool slowly at room temperature. Surface morphology was analyzed by Surface Electron Microscopy (SEM) model LEO (440), with a resolution of 1.5 μm at 30 kV.

Results and discussion:

Scanning Electron Microscopy:

The surface morphological investigations of the compounds Mg_2TiO_4 were explored by SEM, revealing the presence of cubic structure of various sizes 1-2μm depending upon the annealing duration. It is well known crystallographic planes that form the surface, determine the shape of compounds and their crystal habits depend on the relative order of surface energy. This leads to the imperfect spherical surface in the final morphology. Curious growth characteristics resembling a spiral like structures result in the large grain of Mg_2TiO_4. Fig. 2 (a-b) in the SEM micrograph which reveals such features on Mg_2TiO_4 samples which was sintered at 1300 ºC for 72 hours. It also clearly demonstrates that how the nucleation of a new step takes place on an atomically smooth surface. These closed spiral growth loops in various shapes have been observed to be embedded invariably in all the large grain of synthesized Mg_2TiO_4.

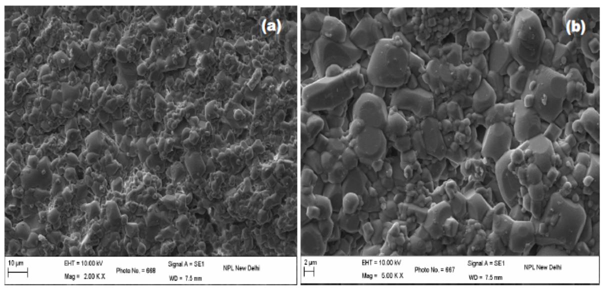

Fig: 2. SEM images of the sample Mg_2TiO_4 with size (a) 10 μm and (b) 2 μm

Magnesium Ortho Titanate (Mg_2TiO_4) prepared by conventional solid state reaction technique, exhibits curious microstructural characteristics in the form of a myriad spiral like growth features. These can be classified as:

1. Single cubic and circular spiral features
2. Interacting and interlaced circular and cubic spiral features
3. Spiral containing inclusion/platelet like features
4. Square spiral features truncated at the corners

A careful analysis of these samples which are sintered at 1300 ºC for 72 hours shows cubical spiral features which are mediated through screw dislocation (fig. 3) [20].

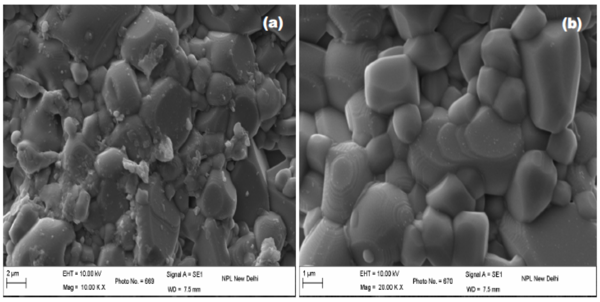

Fig: 3. SEM images of the sample Mg_2TiO_4 with size (a) 2 µm and (b) 1 µm

Possible mechanism for the generation of spiral like growth features of Mg_2TiO_4:

The introduction mechanism of dislocation in high temperature materials is not yet understood. It is expected that control of the density of dislocations will be important for high current device applications. One important condition of the spiral like growth is the sintering temperature as well as the calcination temperature during the solid state reaction technique. Fig. 4 is the magnified image of fig. 3 (b) which clearly shows the cubical growth as well as screw dislocation. It was expected that the growth is totally cubic in structure. It may be possible that when the two growth fronts corresponding to $Mg(NO_3)_2.6H_2O$ and TiO_2 would develop sufficiently and meet each other over an earlier grown structure, a screw dislocation would form due to incoherent meeting. At this stage, it is not possible to pinpoint as to which of the above mechanisms may be operating. However, regardless of the details of the mechanism, it is certain that the material after the initial developments in the form of crystallites (Cubic) develop further through spiral growth mechanism.

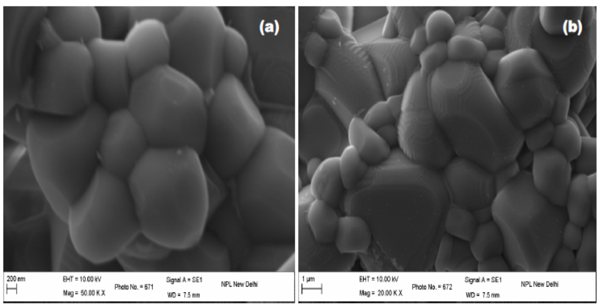

Fig: 4. SEM images of the sample Mg_2TiO_4 with size (a) 200 nm and (b) 1 µm

Conclusions:

The curious growth pattern in the form of growth spirals was found to be associated with the formation of Mg_2TiO_4, inverse spinel compounds. By SEM micrographs, it is established that the growth of the materials occurred by screw dislocation- mediated mechanism. These observations are compatible with a screw dislocation generation mechanism involving the incoherent coalescence of the growth fronts formed from $Mg(NO_3)_2.6H_2O$ and TiO_2 nuclei.

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References:

1. Hazen R. M., (1993)., Comparative compressibilities of silicate spinels: Anomalous behavior of $(Mg,Fe)_2SiO_4$, Science. 259 (259): 206-209.
2. Hayakawa T., Shimada D and Tsuda N., (1989)., Metal insulator transition in $LiTi_{2-x}V_xO_4$, J. Phys. Soc. Jpn. (58): 2867-2876.
3. Johnston D. C., Prakash H, Zachariasen W. H., Viswanathan R., High temperature superconductivity in the $Li_{1+x}Ti_{2-x}O$ ternary system, Matt. Res. Bull. (8): 777-784.
4. Kondo S., Johnson D. C., Swenson C. A., Borsa F., Mahajan A. V., Miller L. L., Gu T., Goldman A. I., Maple M. B., Gajewski D. A., Freeman E. J., Dilley N. R., Dickey R. P., Merrin J., Kojima K., Luke G. M., Uemura Y. J., Chmaissem O. and Jorgensen J. D., (1997)., LiV_2O_4: A heavy fermion transition metal oxide, Phys. Rev. Lett. (78): 3729- 3732.
5. Fujiwara N., Yasuoka H. and Ueda Y., Anomalous spin fluctuation in vanadium spinel LiV_2O_4 studied by ^{7}Li- NMR, Phys. Rev. B. (57): 3539-3542.
6. Urano C., Nohara M., Kondo S., Sakai F., Takagi H., Shiraki T. and Okubo T., (2000)., LiV_2O_4 spinel as a heavy mass Fermi liquid: Anomalous transport and role of geometrical frustration, Phys. Rev. Lett. (85): 1052-1055.
7. Matsuno K., Katsufuji T., Mori S., Moritomo Y., Machida A., Nishibori E., Takata M., Sakata M., Yamamoto N. and Takagi H., (2001)., Charge ordering in geometrically frustrated spinel AlV_2O_4, J. Phys. Soc. Jpn. (70): 1456-1459.
8. Canals B. and Lacroix C., (1998)., Pyrochlore antiferromagnet: A three dimensional quantum spin liquid, Phys. Rev. Lett. (80): 2933-2936.

9. Lee S. H., Broholm C., Kim T. H., Ratcliff W. and Cheong S. W., (2000)., Local spin resonance and spin peierls like phase transition in geometrically frustrated antiferromagnets, Phys. Rev. Lett. (84): 3718-3721.

10. Singh A. K., Kumar R., Senguttuvan T. D., and Siddiqui A. M., (2011)., Synthesis and structural analysis of Al-doped qandilite (Mg_2TiO_4), AIP Conf. Proc. (1393): 235-236.

11. Romein F.C., Physical and crystallographic properties of some spinels, Philips Res. Rep. (78): 304-342.

12. Haefke H., Lang H. P., Sum R., Guntherodt H. J., Berthold L. and Hesse D., (1992)., Mg_2TiO_4 as a nobel substrate for high temperature superconducting thin films, Appl. Phys. Lett. (61): 2359-2362.

13. Matsushita Elec. Ind. Co., Ltd., Jpn. Pat. Appl. No. 81/71743.

14. Lope M. J. M., M. P. B. Pena and M. E. G. Clavel, (1992)., The composition of magnesium titanates as a function of the synthesis methods, Therm. Acta. (194): 247-252.

15. Subotic B., and Bronic J., (2003), Handbook of Zeolite Science and Technology*,* Marcel Dekker, New York, pp. 1184.

16. Hawley M., Raistrick I. D., Berry J. C., Houlton R. J., (1991)., Growth mechanism of sputtered films of $YBa_2Cu_3O_7$ studied by scanning tunneling microscopy, Science (251): 1587-1589.

17. Frank F. C., (1949)., Discuss, The influence of dislocation on crystal growth, Faraday Soc. (5): 48-54.

18. Buston W. K., Canbera N., Frank F. C., (1951)., The growth of crystals and the equilibrium structure of their surfaces, Philos Trans. R. Soc. (A 243): 299-358.

19. Verma A. R., Krishna P., (1996)., Polymorphism and polytypism in Crystal, John Wiley & sons Inc. New York.

20. Schlom D. G., Anselmetti D., Bednorz J. G., Broom R. F., Mannhart A. J., (1992)., Screw dislocation mediated growth of sputtered and laser ablated $YBa_2Cu_3O_{7-\sigma}$ films, Z. Phys. B: Condens. Matt. (86): 163-175.