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Subsolidus Phase Relations in the BaO-TiO₂-Fe₂O₃ System

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Abstract. The subsolidus phase equilibrium relation in the BaO-TiO₂-Fe₂O₃ system at 1240°C in air has been investigated by conventional solid state reaction techniques and X-ray powder diffraction. Twelve quarternary compounds were recognized, BaTi_{1-x}Fe₂O_{3-x} (0.1<x<0.75) (N), Ba₃TiFe₁₀O₂₀ (K), BaTi₂Fe₄O₁₁ (R), Ba₂Ti₄Fe₂O₁₃ (J), Ba₃Ti₄₋₂, Fe₂O₈ (0.55<x<0.67) (H), Ba₁₂Ti₁₆Fe₃₀O₈₉ (I), Ba_{3.5}Ti₅Fe₂₃O₄₈ (O), Ba_{1.8}Ti_{4.4}Fe_{1.36}O₃₁ (L), BaTi₂O₅ (0.2 mol% Fe₂O₃) (Q), Ba₂Ti_{4.73}Fe_{0.27}O_{11.865} (P), Ba₅Ti₁₃Fe₂O₃₄ (A), and Ba₈Ti₁₆Fe₆O₄₉ (B). The phases J, I, O, L, Q, P, A and B are new compounds found in this study. Oxidation of Fe³⁺ to Fe⁴⁺ was observed in the BaO rich region (50 mol%). Ba₁₂Ti₁₆Fe₃₀O₈₉ (I) is a ferrimagnet with a T_c around 130°C.

1. INTRODUCTION

Phase diagrams of the BaO-TiO₂ [1] and BaO-Fe₂O₃ [2] systems were intensively investigated, because certain compounds in these systems find applications as dielectric or magnetic materials. In the extended BaO-TiO₂-Fe₂O₃ system, the existence of quarternary compounds $BaTi_2Fe_4O_{11}$ (R) [3], $Ba_3TiFe_{10}O_{20}$ (K) [4] and hollandite type $Ba_xTi_{4-2x}Fe_{2x}O_8$ [5] is known, but the phase diagram has not been reported systematically.

The BaO-TiO₂-Fe₂O₃ system is interesting from the viewpoint of crystal chemistry and solid state chemistry, because it thus contains several interesting materials crystallizing in a variety of structures. Ba atoms are surrounded by twelve oxygen ions rather symmetrically in the Fe₂O₃-rich region as in BaFe₁₂O₁₉ and R, while they occupy eight-coordinated sites with two open opposite faces in the TiO₂-rich region as in hollandite. Usually Ti⁴⁺ ions are octahedrally coordinated by oxygen, while Fe³⁺ ions can be coordinated either octahedrally or tetrahedrally, or even bipyramidally in same rare cases. The radii of Ti⁴⁺ and Fe³⁺ ions are similar to each other for octahedral cooradination, but these octahedra are linked with each other in a flexible way depending upon the Fe³⁺ and Ti⁴⁺ contents. These suggest that the possible existence of new other quarternary compounds. The purpose of this work is to establish the phase diagram of the BaO-TiO₂-Fe₂O₃ system.

2. EXPERIMENTAL

Starting materials used for the preparation of specimens were $BaCO_3$, TiO_2 , and α -Fe₂O₃ (>99.5% pure each). These were thoroughly mixed in an agate mortar. The mixtures (about 20g each) were pressed into disks, placed on Pt-foils, and calcined at 1000°C in air for one day. After cooling, the reaction mixtures were ground and again pressed into disks. These were heated at 1240°C±5°C in air repeatedly with intermittent grinding and pelletization until their X-ray diffraction patterns did not change any more. The total heating time was at least 3 days, but for some cases it was extended to 1 week. Each heating treatment was followed by rapid cooling to room temperature. Approximately 400 different compositions were examined. Phase identification was carried out by means of X-ray powder diffraction (XRD, Rigaku RAD Ru-200) using graphite monochromated CuK α and CuK β radiations. Lattice parameters of monophasic samples were determined by XRD using Si powder as an internal standard. Microstructures were studied with electron diffraction (ED) and transmission electron microscopy (TEM). Magnetic properties were measured using a Faraday magnetic balance and a vibrating sample magnetometer (VSM). Oxidation state of iron was determined by Mössbauer effect (ME) using a ⁵⁷Co/Rh source.

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3. RESULTS

In the BaTi₂O₃-TiO₂ system Ba₆Ti₁O₄₀, Ba₄Ti₁O₃₀, BaTi₄O₉ and Ba₂Ti₉O₂₀ were formed at 1240°C in air, while BaTi₂O₅, Ba₂Ti₅O₁₂ and BaTi₃O₁₁ were not found. In the Fe₂O₃-TiO₂ system only Fe₂TiO₅ could be detected. In the BaO-Fe₂O₃ system, BaFeO₂₅₊₄, BaFe₂O₄ and BaFe₁₂O₁₉ were formed. In addition to these, twelve quarternary compounds were found in the BaO-TiO₂-Fe₂O₃ system.

The tie-lines between these phases are drawn in Fig. 1. There are 30 compatibility triangles in the composition range of less than 50 mol% BaO. No appreciable solid solubility was found in all the quasi-binary joins: It is only phases H and N that allow the metallic composition to vary within the same structural framework. The cell parameters of the twelve quarternary compounds and their compositions are listed in Table I. The compositions of compounds I, O, B, A, P, and Q were not directly determined. Instead, a triangulation procedure was employed as follows. By varying sample compositions precisely in a narrow range, the appearance and change of a third phase was examined carefully by XRD experiments. The tie-lines were thus established, and the final compositions of the above compounds were determined from the crossing points of these tie-lines. However, these results need be supported by crystal structure analysis in the future. In the triangular region cornered by BaTiO₃, BaFeO_{2.5}, and BaFe₂O₄, BaFe₂O₄ and a hexagonal perovskite phase, N, appeared. According to ME, however, solid-solution N contained iron partially oxidized from Fe³⁺ to Fe⁴⁺. So, the phase relation in this area remained inconclusive. The details of these new compounds will be reported elsewhere in the near future.



Figure 1 The subsolidus phase equilibrium diagram in the BaO-TiO₂ Fe₂O₃ system at 1240°C in air.

Table I The cell parameters of the twelve quarternary compounds and their compositions

| Symbol | Composition | System | a (Å) | b (Å) | c (Å) | ß (deg.) |
|--------|------------------------|------------|--------|--------|---------|----------|
| R | BaTi,Fe,O, | Hex. | 5.843 | | 13.604 | |
| I | Ba, Ti Fe Os | Hex. | 10.008 | | 113.726 | |
| 0 | Ba, Ti Fe, O48 | Hex. | 10.078 | | 182.48 | |
| L | Ba, Ti, Fe, Ou | Monocli. | 19.463 | 20.340 | 10.100 | 105.375* |
| J | Ba, Ti, Fe, O13 | Monocli. | 15.267 | 3.893 | 9.150 | 98.48° |
| Н | Ba Ti, Fe, O, | Monocli. | | | | |
| | 0.55 < x < 0.67 | x = 0.67 | 10.219 | 2.979 | 9.961 | 90.849° |
| в | Ba, Ti, Fe, O, | Hex. | 9.99 | | 42.27 | |
| А | Ba, Ti, Fe, O, | Ortho. | 32.403 | 23.131 | 11.446 | |
| Р | Ba, Ti, FennO. | Ortho. | 23.34 | 11.367 | 9.93 | |
| Q | BaTi,O, (0.2mol% Fe,O, |) Monocli. | 16.89 | 3.93 | 9.41 | 103.03° |
| К | Ba, TiFe10O20 | Monocli. | 15.353 | 11.834 | 5.1835 | 86.53° |
| N | BaTi, Fe O | Hex. | | | | |
| | 0.1 < x < 0.75 | x = 0.68 | 5.73 | | 14.05 | |

References

- [1] T. Negas, R.S. Roth, H.S. Rarker and D. Minor, J. Solid State Chem., 9, 3 (1974) 297-307.
- [2] Y. Goto and T. Takada, J. Am. Ceram. Soc., 43, 3 (1960) 150-153.
- [3] F. Haberey and M. Velicescu, Acta Crystallogr., B30, (1974) 1507.
- [4] M.C. Cadèe and D.J.W. Ijdo, J. Solid State Chem., 41 (1982) 39-43.
- [5] M.C. Cadèe and G.C. Vershoor, Acta Cryst., B34 (1978) 3554-3558.