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Tolerance factor and the stability discussion of ABO_3-type ilmenite

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Abstract The tolerance factor of ABO_3-type ilmenite by analyzing the ABO_3 ilmenite crystal structure is established. Combining with the electronegativity difference and octahedral factor of ABO_3 structure, regularities governing the formation and the stability of ilmenite-type compounds are discussed. The tolerance factor equation was proved appropriate for ilmenite structure by analyzing the structure stability of some ilmenite compounds. According to the results of statistically analyzing the tolerance factor and electronegativity difference of the present ABO_3-type ilmenite, the experience tolerance factor value and experience electronegativity difference value to form stable ilmenite compound were obtained, that is, $t > 0.80$ and $e > 1.465$, and the lowest limit of the octahedral factor $(R_M/R_{O^{2-}})$ for ilmenite formation is 0.48.

1 Introduction

In the past several decades, special attentions have been paid to the ABO_3 ilmenite-type oxides because they have excellent dielectric, piezoelectric, pyroelectric and photostrictive properties and expected wide range of applications. They can be used as dielectric, piezoelectric, pyroelectric, optoelectrical [1], gas-sensing [2, 3] and lithium ion battery materials [4]. But the thermal stability of ABO_3 ilmenite-type oxides often affect their used properties because some of them transform to perovskite structure [5] or decompose to spinel structure and rutile [6]. On the other hand, the thermal stability of ABO_3 ilmenite-type oxides can be promoted by forming ABO_3 ilmenite-type solid solution of different ABO_3 ilmenite. For example, $ZnTiO_3$ ilmenite will decompose to rutile and Zn_2TiO_4 when the sintering temperature is above 900 °C, but the stability region of ilmenite phase extend from 900 to 1,150 °C in (Zn, Mg)TiO_3 ilmenite-type solid solution [7]. It is of interest to find out regularities governing the formation of ilmenite-type compounds and use it to further guide the exploration of new materials. It is well known that in early 1920s, Goldschmidt [8] has proposed a "tolerance factor" $(t = (R_A + R_O)/\sqrt{2}(R_B + R_O)$ (where R_A, R_B and R_O are the ionic radii of A, B and O, respectively) to study the stability of perovskites. Tolerance factor [9] is a geometry parameter describing the mismatch of A- and B-site ions in the compound, as was demonstrated by Hwang et al. [10] and Teresa et al. [11].

Up to now, Goldschmidt's tolerance factor t has been widely accepted as a criterion for the formation of the perovskite structure, a number of researchers have used it to discuss the perovskite stability, including oxides [12–15], fluorides [16, 17], chlorides [8]. In this paper, we attempt to establish the tolerance factor of ABO_3-type ilmenite by analyzing the ABO_3 ilmenite crystal structure, and to find out regularities governing the formation of ilmenite-type compounds combining with the electronegativity difference and octahedral factor of ABO_3 structure. In addition, some ilmenite compounds such as $MgTiO_3$, $NiTiO_3$, $CoTiO_3$, $ZnTiO_3$, and complex ilmenite (Zn_{1-x}, M_x)TiO_3 (M denote Mg, Ni, Co) are used to verify the reasonableness of established tolerance factor.

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2 Experimental procedure

$MTiO_3$ and $(Zn_{1-x}M_x)TiO_3$ ($x = 0$ to $x = 1$, M denote Mg, Ni, Co) powder were prepared by using a semichemical rout respectively. The A.R zinc hydroxide carbonate ($Zn_5(CO_3)_2 \cdot (OH)_6$), A.R magnesium hydroxide carbonate ($Mg(OH)_2 \cdot 4MgCO_3 \cdot 6H_2O$), A.R. NiO, A.R. CoO and anatase (TiO_2, 10–30 nm) were used as raw materials. Firstly, the carbonates were heat-treated at 350 and 540 °C for 2 h in air to obtain nanopowder ZnO (10–30 nm) and MgO (20–50 nm) with high active energy as starting materials, respectively. X-ray diffractometry (XRD) confirmed that pure phase ZnO and MgO were obtained. Then anatase nanopowder was mixed with ZnO, MgO, NiO and CoO using planetary milling with zirconia balls in ethanol for 24 h, respectively. At last, the mixture was dried and then calcined at 1,000 °C for 2 h. The phase structure of the samples was investigated using XRD (X′ Pert MPD PRO, Holland).

3 Results and discussion

The ABO_3-type ilmenite has an ordered corundum structure, where each AO_6 octahedron layer is sandwiched by two BO_6 octahedron layers, which is a modified α-Al_2O_3 structure, as indicated in Fig. 1a [18]. In every octahedron, faces are shared along the *c*-axis, edges are shared in the *ab*-plane and apices are shared along the oblique direction. One pair of edge-shared AO_6 octahedron is isolated by the C cation vacancies in the *ab*-plane and is separated by the BO_6 octahedron along the oblique directions. It is very difficult to deduce the tolerance factor of ilmenite from such complex sharing types. From another angle of view, ilmenite titanate structure can be shown as Fig. 1b. Connecting the centre atom in one pair of plane-shared TiO_6 octahedron (such as A and C (cation vacancy) in Fig. 1a) to the three O atoms in the sharing plane, a hexahedron with A and C as apex (express as ACO_3 hexahedron) forms, which is shown a shadow part in Fig. 1a. In like manner, another hexahedron with A and B as apex (express as ABO_3 hexahedron) forms which is apex-shared with the former hexahedron. The rest can be deduced by analogy, the ilmenite structure can be characterized as an apex-shared hexahedron structure, as shown in Fig. 1b.

In AO_6 octahedron, the geometrical relationship of ion A and O^{2-} can be shown as expression (1):

$$\sqrt{2}R_{O^{2-}} = R_{O^{2-}} + R_A \tag{1}$$

In like manner, the geometrical relationship of ion B and O^{2-} and the geometrical relationship of C and O^{2-} can be shown as expression (2) and expression (3), respectively:

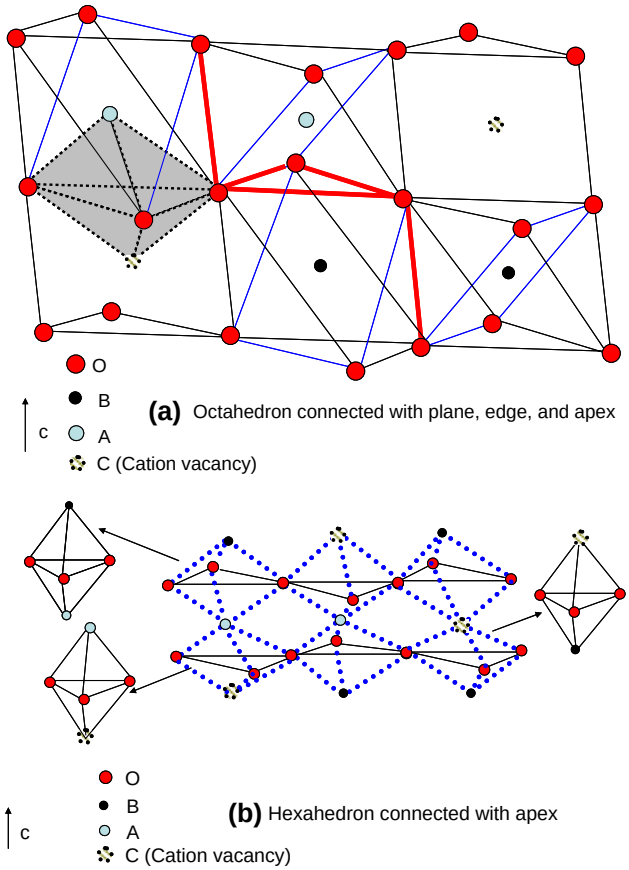

Fig. 1 Schematic crystal structure of ilmenite titanates

$$\sqrt{2}R_{O^{2-}} = R_{O^{2-}} + R_B \tag{2}$$

$$\sqrt{2}R_{O^{2-}} = R_{O^{2-}} + R_C \tag{3}$$

In above three expressions, R_A, R_B, and $R_{O^{2-}}$ denote the radius of ion A, ion B, and O^{2-}. R_C represents dummy equivalent radius of C cation vacancies.

According to Fig. 1b, the geometrical relationship of the hexahedron with A and B as apex can be shown as expression (4):

$$R_{O^{2-}} + R_B = R_{O^{2-}} + R_A \tag{4}$$

As we know, the size of ion A and/or B will not satisfy expression (4) at the right moment, it would be slightly big in or small in the size of ideal R_A and/or R_B. Therefore, a tolerance factor t_1 is introduced into expression (4), and we obtain expression (5):

$$t_1 = (R_{O^{2-}} + R_B)/(R_{O^{2-}} + R_A) \tag{5}$$

In like manner, expressions (6) and (7) can be deduced

$$t_2 = \sqrt{2}R_{O^{2-}}/(R_{O^{2-}} + R_A) \tag{6}$$

$$t_3 = \sqrt{2}R_{O^{2-}}/(R_{O^{2-}} + R_B) \tag{7}$$

Because there three hexahedrons, ABO_3 hexahedron, ACO_3 hexahedron and BCO_3 hexahedron, all have the same occupancy in ilmenite structure, the tolerance factor t of ABO_3-type ilmenite can be shown as follow:

$$t = (t_1 + t_2 + t_3)/3 = \frac{1}{3}\left(\frac{(\sqrt{2}+1)R_{O^{2-}} + R_B}{R_{O^{2-}} + R_A} + \frac{\sqrt{2}R_{O^{2-}}}{R_{O^{2-}} + R_B}\right) \quad (8)$$

Above deducing procedure is based on three hypotheses: (1) hard-sphere model; (2) close-packed crystal; (3) ideal ilmenite structure.

$MgTiO_3$, $NiTiO_3$, $CoTiO_3$, $ZnTiO_3$ are all typical ilmenite compounds. And they are easy to be prepared by conventional solid-state reaction method. The third, Refs. [7, 19–22] have implied the thermal stability sequence of them. Hence, to verify the reasonableness of tolerance factor t, the stabilities of $MgTiO_3$, $NiTiO_3$, $CoTiO_3$, $ZnTiO_3$, and complex ilmenite $(Zn_{1-x}, M_x)TiO_3$ (M denote Mg, Ni, Co) are investigated.

Figure 2 shows the XRD patterns of $ZnTiO_3$, $MgTiO_3$, $CoTiO_3$, $NiTiO_3$ calcined at 1,000 °C. At 1,000 °C, $ZnTiO_3$ has decomposed completely to rutile and Zn_2TiO_4; the appearance of small amount of Co_2TiO_4 suggests part of $CoTiO_3$ has decomposed; $NiTiO_3$ is not synthesized completely, because residues are also NiO and TiO_2; only $MgTiO_3$ is synthesized completely, and no phase decomposition. These results show the thermal stability sequence of $ZnTiO_3$, $MgTiO_3$, $CoTiO_3$, $NiTiO_3$ is $MgTiO_3 > NiTiO_3 > CoTiO_3 > ZnTiO_3$. According to the expression (8), the value of t is calculated. The t sequence of four compounds is $MgTiO_3$ (t = 0.9620) > $NiTiO_3$ (t = 0.9523) > $CoTiO_3$ (t = 0.9429) > $ZnTiO_3$ (t = 0.9367) which is consistent with the thermal stability sequence [7, 19–22].

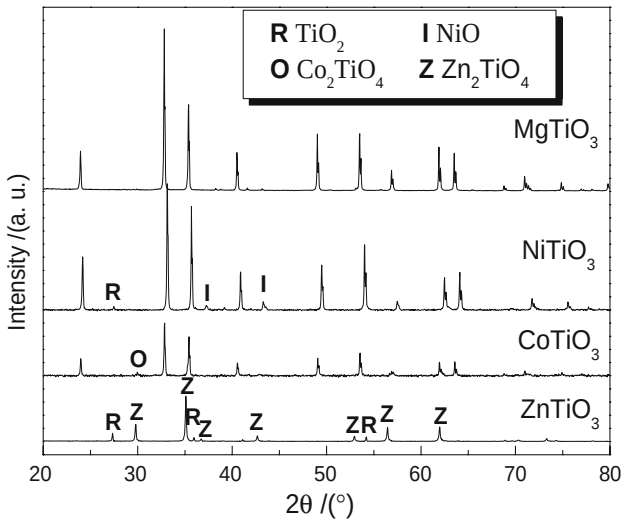

Fig. 2 XRD patterns of $ZnTiO_3$, $MgTiO_3$, $CoTiO_3$, $NiTiO_3$ calcined at 1,000 °C

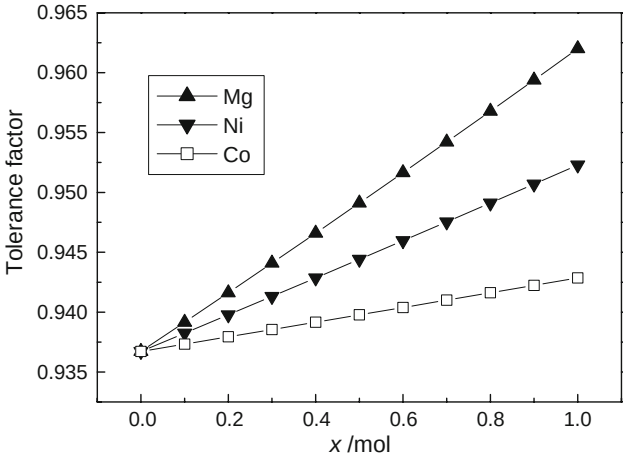

Fig. 3 The tolerance factor of $(Zn_{1-x}, M_x)TiO_3$ vs. x (M: Mg, Ni, Co)

Figure 3 shows the tolerance factor of $(Zn_{1-x}, M_x)TiO_3$ solid solutions (M: Ni, Co, Mg). The tolerant factor of three solid solutions, $(Zn_{1-x}, Mg_x)TiO_3$, $(Zn_{1-x}, Ni_x)TiO_3$ and $(Zn_{1-x}, Co_x)TiO_3$, all increase with x increasing. This result suggests that substituting M for Zn improve the stability of $ZnTiO_3$ ilmenite, which corresponds with the reports of other researchers.

Above results prove the reasonableness of tolerance factor of ABO_3-type ilmenite. But it is important to point out that the tolerance factor t is only a necessary but not a sufficient condition for the formation of the ilmenite structure. Another necessary condition is electronegativity difference (abbreviated to e) of the present ABO_3-type ilmenite. The electronegativity difference provides a measure of the excess binding energy between atoms A and B, the greater the electronegativity difference, the greater the excess binding energy [23]. So it can be deduce that the greater the electronegativity difference, the higher the stability of ilmenite structure. This law is similar to perovskite structure [23]. The tolerance factor and electronegativity difference of almost reported ABO_3-type ilmenite [5, 18, 24–31] compounds have been calculated, the results are shown in Fig. 4. The criterion of ABO_3-type ilmenite formability is expressed by the following equations:

$$t = (t_1 + t_2 + t_3)/3 = \frac{1}{3}\left(\frac{(\sqrt{2}+1)R_{O^{2-}} + R_B}{R_{O^{2-}} + R_A} + \frac{\sqrt{2}R_{O^{2-}}}{R_{O^{2-}} + R_B}\right) > 0.8 \quad (9)$$

$$e > 1.465 \quad (10)$$

Additional parameters may be necessary for the prediction of ilmenite formation. It is well known that [32] the octahedron MO_6 is the basic mosaic or unit for

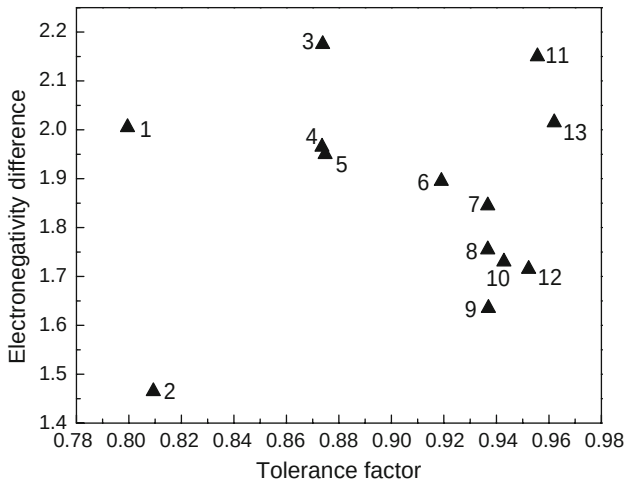

Fig. 4 Tolerance factor and electronegativity difference of some ABO_3 compounds (1-$KSbO_3$, 2-$AgBiO_3$, 3-$NaNbO_3$, 4-$NaBiO_3$, 5-$NaSbO_3$, 6-$MnTiO_3$, 7-$ZnTiO_3$, 8-$FeTiO_3$, 9-$ZnSnO_3$, 10-$CoTiO_3$, 11-$LiNbO_3$, 12-$NiTiO_3$, 13-$MgTiO_3$)

ilmenite structure. If one cation and six anions form an octahedron, the ratio of their ionic radius $(R_M/R_{O^{2-}})$ is within a limited range [23], this factor is defined as the octahedral factor.MO_6 is the basic unit, if ion M is too small, this unit may become unstable. So does the ilmenite. This can also be better explained by the ratio of cation and anion size, R_c/R_a, in the octahedron. The reported lowest limit of R_c/R_a for octahedron [23] is 0.414. In our calculated value of R_c/R_a of the ABO_3-type ilmenite shown in Fig. 4, the lowest limit of the octahedral factor $(R_M/R_{O^{2-}})$ for ilmenite formation is 0.48, these two values agree with each other well. That is, the third condition for the formation of the ilmenite structure is

$$\frac{R_M}{R_{O^{2-}}} \geq 0.48 \tag{11}$$

Above mentioned three conditions are only the empirical value, and are only necessary but not sufficient conditions for the formation of the ilmenite structure. In fact, pure phase of most ilmenite compounds are difficult to be prepared by conventional solid-state reaction method, mainly is because the octahedron connection mode difference. Pauling's third rule [23] tells us how to link the polyhedra together. Corners rather than faces or edges tend to be shared in stable structures. In ilmenite, this is due to the fact that the cation separation between adjacent octahedron decreases as edges and faces are shared, increasing repulsion and leading to unstable structures. By using tolerance factor, some new method to improve the stability of ilmenite can be sought. For example, substituting Mg, Ni and Co for Zn improve the stability of $ZnTiO_3$ ilmenite. In addition, the mentioned three conditions can be used to search for new ilmenite, and may assist in the design of new materials.

4 Conclusions

By analyzing ABO_3-type ilmenite crystal structure, we established its tolerance factor calculation formula. And combining with the electronegativity difference and octahedral factor of ABO_3 structure, we discussed ABO_3-type ilmenite of formation regulation and stability regulation. The tolerance factor equation was proved appropriate for ilmenite structure by analyzing the structure stability of some ilmenite compounds such as $MgTiO_3$, $NiTiO_3$, $CoTiO_3$, $ZnTiO_3$ and complex ilmenite $(Zn_{1-x}, M_x)TiO_3$ (M denote Mg, Ni, Co). According to the results of statistical analyzing the tolerance factor and electronegativity difference of the present ABO_3-type ilmenite, the experience tolerance factor value and experience electronegativity difference value to form stable ilmenite compound were obtained, that is, $t > 0.80$ and $e > 1.465$, and the lowest limit of the octahedral factor $(R_M/R_{O^{2-}})$ for ilmenite formation is 0.48.

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References

1. J.D. Perkins, J.A. del Cueto, J.L. Alleman, C. Warmsingh, B.M. Keyes, L.M. Gedvilas, P.A. Parilla, B. To, D.W. Readey, D.S. Ginley, Thin Solid Films **411**, 152–160 (2002). doi:10.1016/S0040-6090(02)00205-5
2. X.H. Wu, Y.D. Wang, Z.H. Tian, H.L. Liu, Z.L. Zhou, Y.F. Li, Solid-State Electron **46**, 715–719 (2002). doi:10.1016/S0038-1101(01)00310-0
3. X.H. Wu, Y.D. Wang, H.L. Liu, Y.F. Li, Z.L. Zhou, Mater. Lett. **56**, 732–736 (2002). doi:10.1016/S0167-577X(02)00604-3
4. Z.Y. Yuan, F. Huang, J.T. Sun, Y.H. Zhou, Chem. Lett. **31**, 408–409 (2002). doi:10.1246/cl.2002.408
5. B. Wang, S.C. Chen, M. Greenblatt, J .Solid State Chem. **108**, 184–188 (1994). doi:10.1006/jssc.1994.1028
6. X.C. Liu, F. Gao, L.L. Zhao, C.S. Tian, J. Alloys Compd. **436**, 285–289 (2007). doi:10.1016/j.jallcom.2006.07.027
7. X.C. Liu, F. Gao, M. Zhao, C.S. Tian, Mater. Sci. Forum **546–549**, 2215–2218 (2007)
8. A.S. Bhalla, R. Guo, R. Roy, Mat. Res. Innovat. **4**, 3–26 (2000). doi:10.1007/s100190000062
9. J.R. Sun, G.H. Rao, J.K. Liang, Appl. Phys. Lett. **70**, 1900–1902 (1997). doi:10.1063/1.118725
10. H.Y. Hwang, S.W. Choeng, R.G. Radaelli, M. Marezio, B. Batlog, Phys. Rev. Lett. **75**, 914–917 (1995). doi:10.1103/PhysRevLett.75.914
11. J.M. de Teresa, M.R. Ibarra, J. Garcia, J. Blasco, C. Ritter, P.A. Algarabel, C. Marguina, A. del Moral, Phys. Rev. Lett. **76**, 3392–3395 (1996). doi:10.1103/PhysRevLett.76.3392
12. E.A. Wood, Acta Cryst. **4**, 353–362 (1951). doi:10.1107/S0365110X51001112
13. J.M. Moreau, Mater. Res. Bull. **3**, 427–432 (1968). doi:10.1016/0025-5408(68)90033-0

14. R.D. Shannon, Inorg. Chem. **6**, 1474–1478 (1967). doi:10.1021/ic50054a009
15. D. Babel, Z. Anorg. Allg. Chem. **369**, 117–130 (1969). doi:10.1002/zaac.19693690303
16. A. Vedrine, J.P. Besse, G. Baud, M. Capestan, Rev. Chim. Miner. **7**, 593–610 (1970)
17. J.H. Sohn, Y. Inaguma, S.O. Yoon, M. Itoh, T. Nakamura, S.J. Yoon, H.J. Kim, Jpn. J. Appl. Phys. **33**, 5466–5470 (1994). doi:10.1143/JJAP.33.5466
18. H.T. Kim, S. Nahm, J.D. Byun, J. Am. Ceram. Soc. **82**, 3476–3480 (1999)
19. H.T. Kim, J.C. Hwang, J.H. Nam, B.H. Choi, M.T. Lanagan, J. Mater. Res. **18**, 1067–1072 (2003). doi:10.1557/JMR.2003.0147
20. H.T. Kim, M.T. Lanagan, J. Am. Ceram. Soc. **86**, 1874–1878 (2003). doi:10.1111/j.1151-2916.2003.tb03575.x
21. Y.R. Wang, S.F. Wang, Y.M. Lin, Ceram. Int. **31**, 905–909 (2005). doi:10.1016/j.ceramint.2004.09.017
22. B.S. Mitchell, *An Introduction to Materials Engineering and Science: For Chemical and Materials Engineers* (Wiley, 2004)
23. X.C. Liu, F. Gao, C.S. Tian, Mater. Res. Bull. **43**, 693–699 (2008). doi:10.1016/j.materresbull.2007.03.029
24. D. Kovacheva, K. Petrov, Solid State Ionics **109**, 327–332 (1998). doi:10.1016/S0167–2738(97)00507-9
25. N. Kinomura, N. Kumada, F. Muto, Mater. Res. Bull. **19**, 299–304 (1984). doi:10.1016/0025-5408(84)90170-3
26. N. Kumada, N. Ozawa, N. Kinomura, F. Muto, J. Solid State Chem. **57**, 267–268 (1985). doi:10.1016/S0022-4596(85)80017-7
27. N. Kumada, N. Kinomura, A.W. Sleight, Mater. Res. Bull. **35**, 2397–2402 (2000). doi:10.1016/S0025-5408(00)00453-0
28. Y. Kong, J. Xu, X. Chen, C. Zhang, W. Zhang, G. Zhang, J. Appl. Phys. **87**, 4410–4414 (2000). doi:10.1063/1.373085
29. V.B. Nalbandyan, M. Avdeev, A.A. Pospelov, Solid State Sci. **8**, 1430–1437 (2006). doi:10.1016/j.solidstatesciences.2006.05.017
30. P.B. Fabritchnyi, M.V. Korolenko, M.I. Afanasov, M. Danot, E. Janod, Solid State Commun. **125**, 341–346 (2003). doi:10.1016/S0038-1098(02)00808-6
31. R.P. Liferovich, R.H. Mitchell, Phys. Chem. Miner. **32**, 442–449 (2005). doi:10.1007/s00269-005-0020-7
32. Z.L. Wang, Z.C. Kang, *Functional and Smart Materials* (Plenum Press, New York, 1998)