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INFLUENCE OF DOPANTS ON STRUCTURE OF POLYCRYSTALLINE BISMUTH NIOBATE

ABSTRACT

Bismuth niobate ($BiNbO_4$) has attracted attention as a low-fired ceramics with promising microwave application potential. $BiNbO_4$ ceramics was fabricated by mixed oxide method and sintered at temperature T<1000˚C. As the sintering aids a small amount of CuO oxide was used. The crystalline structure of the ceramic samples was examined by X-ray diffraction method at room temperature. The Rietveld refinement method was used for analysis of diffraction data. As a result an influence of dopants on crystal structure of bismuth niobate ($BiNbO_4$) ceramics was revealed. It was found that fabricated $BiNbO_4$ ceramics adopted the orthorhombic symmetry (α-$BiNbO_4$ phase, *Pnna* (52) space group). Small differences in elementary cell parameters were found.

Keywords*: $BiNbO_4$ ceramics, X-ray diffraction, phase analysis, crystal structure*

INTRODUCTION

Rapid development of the mobile telecommunication has caused an increasing effort towards further miniaturization of microwave devices [1]. In order to miniaturize devices of band pass filters and antenna duplexers, multilayer microwave devices have been investigated. Realization of these devices may be accomplished by integration of passive components such as capacitors, resistors, inductors and line resonators into the substrate carrying the integrated circuits. In this connection it should be noted that such "passive integration" is performed using multilayer ceramics technology, whereby green ceramic tapes of different materials are laminated and co-fired usually at rather low temperatures (T<1000˚C) with low loss and low melting point electrode such as Ag or Cu [1].

For microwave ceramics, it is desirable to have a high dielectric constant, a small temperature coefficient of resonant frequency, and high quality factor. The dielectric constant determines the size of the dielectric resonator operating at a given frequency, the temperature coefficient of resonant frequency expresses the variation of resonant frequency with the change in temperature, and the quality factor is the figure of merit, which reflects the dielectric loss of ceramics and is inversely proportional to bandwidth [2].

On the other hand, most of the known commercial microwave dielectrics such as complex perovskite compounds: $Sn_xZr_{1-x}TiO_3$, $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) that exhibit excellent microwave dielectric properties, can be sintered only at very

high temperatures greater than 1400˚C. Therefore, it is necessary to find the microwave dielectric ceramics with low sintering temperatures. An extensive overview of most known microwave dielectric materials is available elsewhere [e.g. 3].

Bismuth niobate ($BiNbO_4$) has been reported to be a promising microwave dielectric due to its high quality factor (Q=14000), small temperature coefficient of resonance frequency (~50 ppm/˚C), and relatively low dielectric constant (~45) [4].

$BiNbO_4$ belongs to the bismutocolumbite oxides with similarly to scheelite-like stibiotantalite structure ($SbTaO_4$) $A^{3+}B^{5+}O_4$. It exhibits a triclinic phase (β), when the sintering temperature is increased above 1020˚C (Fig. 1a) and an orthorhombic structure (α) when the sintering temperature is about 900˚C (Fig. 1b) [5].

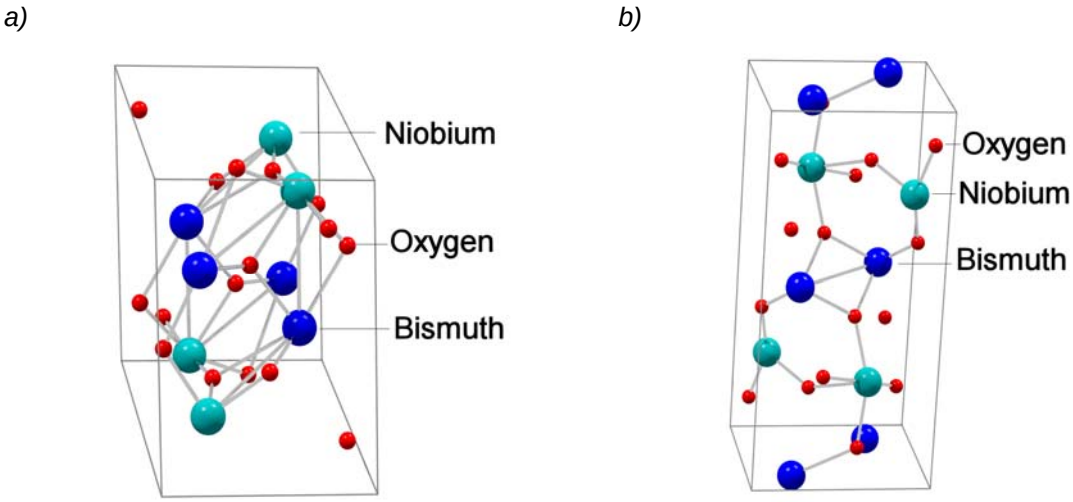

Fig. 1. Models of $BiNbO_4$ crystal structure for the high-temperature triclinic β-phase (a) and the low-temperature orthorhombic α-phase (b)

It is worth noting that various attempts have been undertaken to improve the microwave dielectric properties of $BiNbO_4$, such as the substitution of lanthanide for Bi [e.g. 6, 7], the solid solutions of $Bi(Nb_{1-x}Ta_x)O_4$, $Bi(Nb_{1-x}Sb_x)O_4$ and the addition of various sintering aids like Bi_2O_3 [8], CuO [9], V_2O_5 [10] or CuO-V_2O_5 mixtures [11, 12]. However, the effect of the additives on structural characteristics of $BiNbO_4$ ceramics was not reported. It is interesting to clarify the above relationship because as it is commonly known [e.g. 13], the crystal structure determines the properties of the materials, especially microwave dielectric properties.

Aim of the present research was to study an influence of CuO dopant on crystal structure of $BiNbO_4$ ceramics fabricated by mixed oxide method followed by pressureless sintering at temperature T<1000˚C.

EXPERIMENTAL

$BiNbO_4$ ceramics used for structural characterization in the present study was synthesized using solid state reaction method from the mixture of oxide powders (mixed oxide method). The appropriate amounts of reagent – grade oxide powders, viz. Bi_2O_3 and Nb_2O_5 were thoroughly weighted in stoichiometric amounts to provide conditions for formation of the desired composition, given in Eq. (1):

$$Bi_2O_3 + Nb_2O_5 \rightarrow 2\ BiNbO_4 \qquad (1)$$

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In the present study four sets of $BiNbO_4$ ceramic samples were fabricated, namely the stoichiometric one, the one containing an an excess of 2.5wt% of CuO.

Then the mixture of oxides was ground with an agate mortar and pestle first. After that the planetary ball mill was utilized for wet grinding of the powders. A small amount of ethyl alcohol and zirconia balls as grinding medium were used in the milling/homogenizing treatment that lasted for t=24h. After milling the powders were subjected for drying. When dried the mixture of powders was compacted into pellets of 20 mm in diameter by pressing under pressure of p=30 MPa in a stainless – steel die. The green bodies were then placed in an alumina crucible and fired with air at T=800□ (the heating rate ˚C /min, the soaking time t=2h) to conduct the solid state reaction. After thermal treatment the pellets were crushed in a mortar and the synthesized material was subjected to wet milling and drying again. Before final sintering the compacts were formed in a stainless – steel die of 10 mm in diameter. Final sintering was performed by pressureless sintering under ambient air in a furnace at temperature T=910˚C and soaking time t=2h. Thus fabricated $BiNbO_4$ ceramics were characterized in terms of phase composition, microstructure and crystal structure. Details of the preparation method as well as results of simultaneous thermal analysis (STA) of the powders, have been reported by us elsewhere [14, 15].

The phase composition as well as the crystal structure of powdered ceramics were studied by X-ray diffraction method at room temperature (XPert – Pro diffractometer, Θ - 2Θ mode, CoKα or CuKα radiation, detector scan step $\Delta 2\Theta$=0.01^0 and a counting time t=100s.). Phase analysis of X-ray diffraction patterns of $BiNbO_4$ powders was carried out using Match! (Crystal Impact) computer program [16].The structural analysis was performed with X'pert HighScore Plus software (PANalytical B.V). The latest available ICSD [17], ICDD [18] and IUCr/COD/AMCSD [19], databases were utilized. Refinement of the structural parameters of $BiNbO_4$ ceramics was performed with the Rietveld method [e.g. 20].

RESULTS AND DISCUSSION

Morphology of $BiNbO_4$ ceramics sintered at Ts=910˚C with stoiciometric composition and with CuO additive are shown in Fig. 2. One can see in from Fig. 2 that CuO additive has a substantial influence on morphology of $BiNbO_4$ ceramics. Application of CuO as a sintering aid decreased porosity of the ceramic samples under study.

a) *b)*

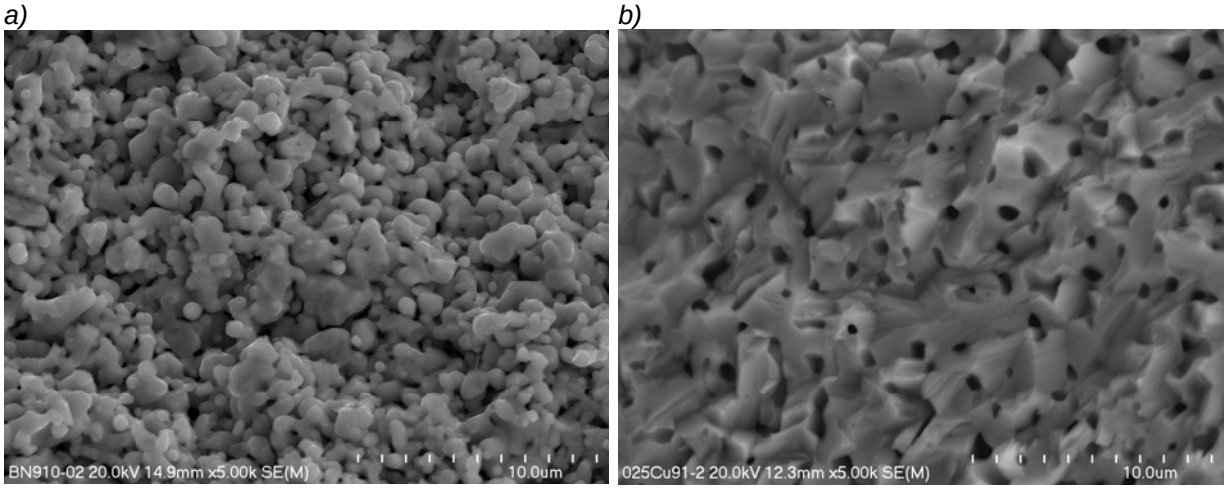

Fig. 2. Morphology of $BiNbO_4$ ceramics sintered at Ts=910°C with stoichiometric composition (a) and with 2.5wt% of CuO additive (b)

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Results of the X-ray phase analysis performed for all compositions under study have proved that $BiNbO_4$ compound with orthorhombic structure was fabricated. As an example Fig. 3 illustrates results of the phase analysis of $BiNbO_4$ ceramics modified with 2.5wt% of CuO.

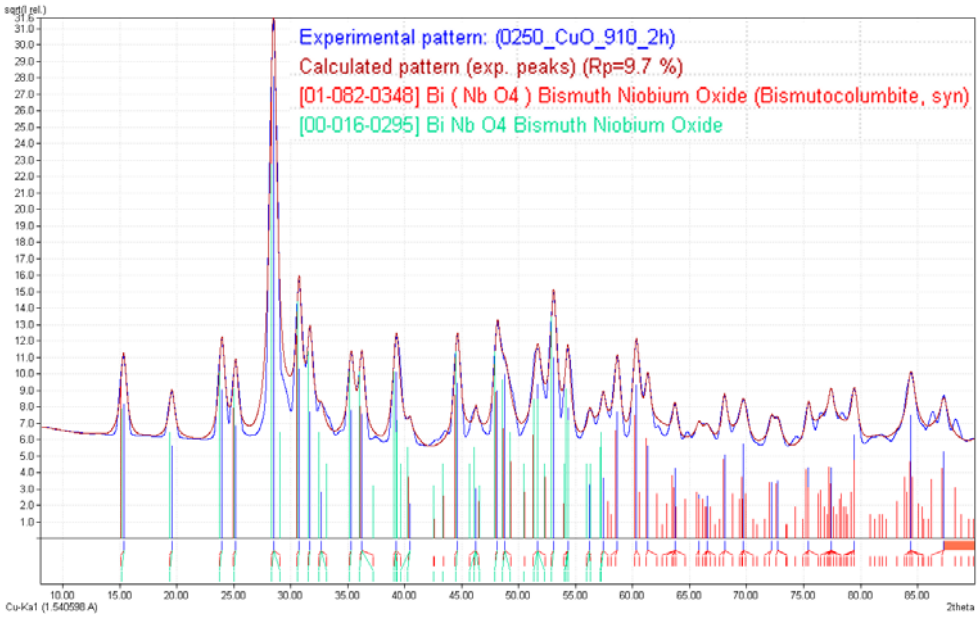

Fig. 3. Results of X-ray phase analysis of $BiNbO_4$ modified with 2.5wt % of CuO oxide. Miler indices (hkl) are not shown to increase visibility of diffraction lines

It should be noted that figure of merit (*FOM* - a number which is calculated from the various measures of agreement between database and unknown pattern) showing quality of the phase identification was *FOM*=83.65% for powder diffraction standard PDF 01-082-0348 (bismutocolumbite, syn) and *FOM*=82.85% for PDF 00-016-0295 (bismuth niobium oxide). The best value of *FOM*=86.89% was achieved for PDF 01-082-0348 standard while $BiNbO_4$ ceramics fabricated from stoichiometric mixture of oxides was studied.

Comparison of X-ray diffraction patterns recorded at room temperature for the samples of $BiNbO_4$ ceramics sintered at T=910˚C without and with CuO additive is given in Fig. 4.

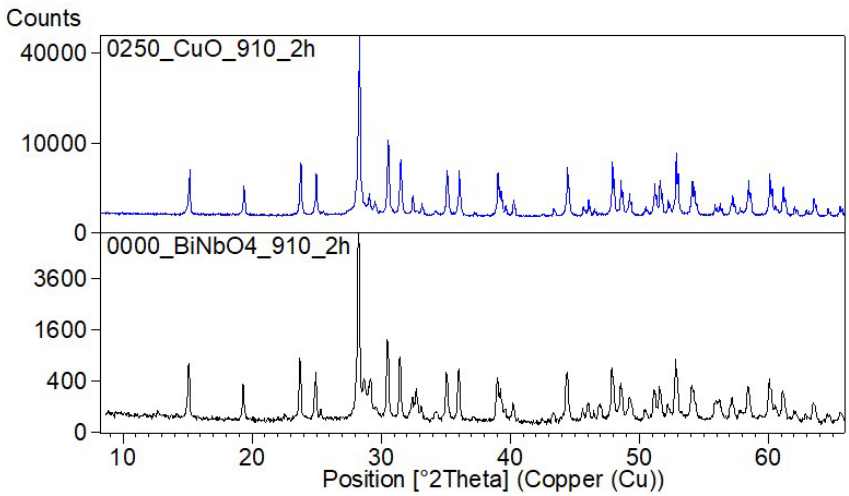

Fig. 4. Comparison of X-ray diffraction patterns of $BiNbO_4$ ceramics sintered at T=910°C with 2.5 wt.% of CuO additive and without any additives (i.e. stoichiometric composition) - from top to bottom, respectively

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One can see from Fig. 4 that X-ray powder diffraction patterns are almost identical. The detailed analysis based on the Rietveld refinement method [20] was performed and the resultant X-ray diffraction pattern for CuO modified $BiNbO_4$ is given in Fig. 5.

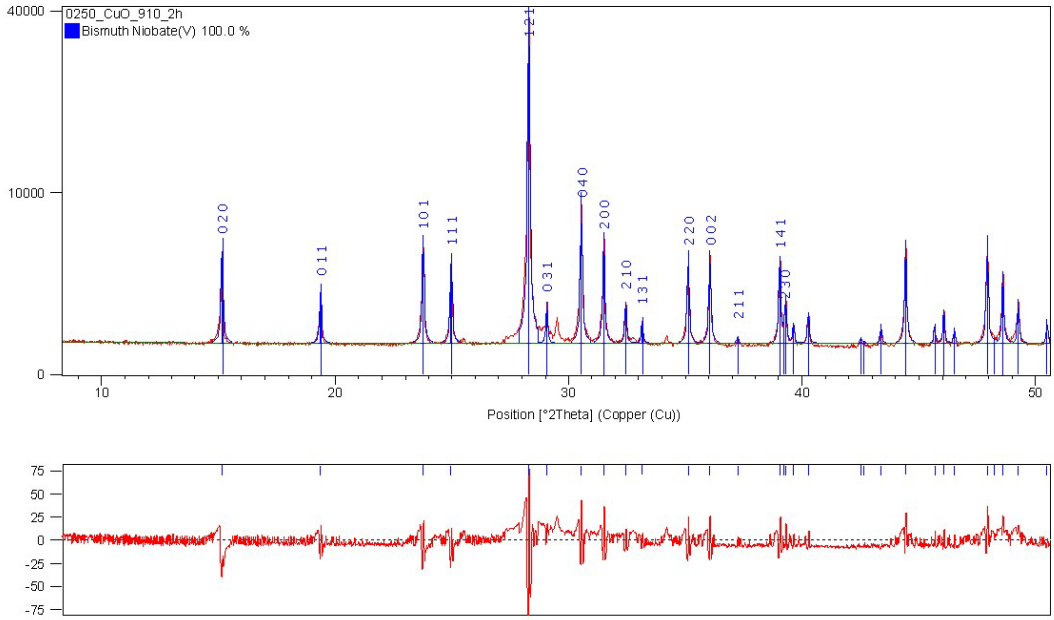

Fig. 5. X-ray diffraction pattern of $BiNbO_4$ ceramics modified with 2.5wt% of CuO oxide

The calculations have shown that $BiNbO_4$ ceramics sintered at T=910˚C without additives as well as with 2.5 wt% of CuO additive exhibits orthorhombic structure described with *Pnna* (52) space group. However, the differences in structural characteristics were found (Fig. 6).

a) *b)*

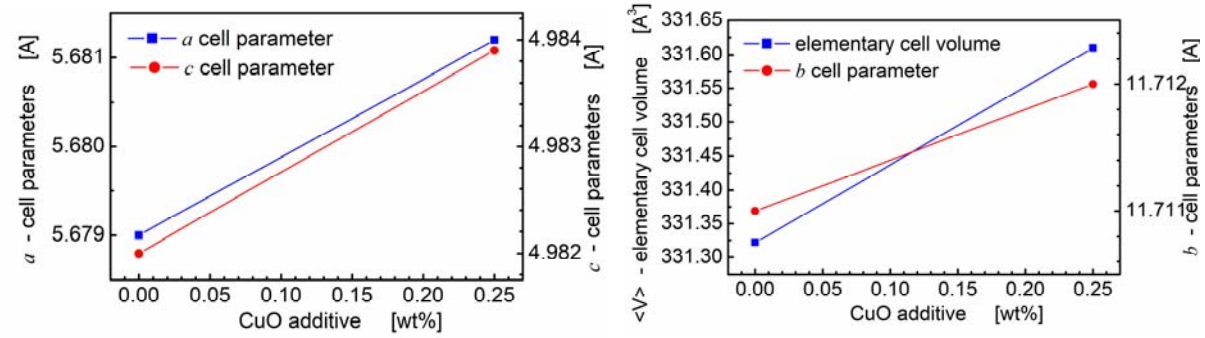

Fig. 6. Dependence of elementary cell parameters and elementary cell volume of $BiNbO_4$ ceramics on CuO additive

One can see from Fig. 6 that 2.5wt% of CuO additive led to an increase in the elementary cell parameters. It means that apart from the sintering aid effect (due to low melting point of CuO) that was visible in a less porous microstructure of the sintered ceramics (Fig. 2) Cu can act as an element substituting either bismuth (Bi) [9] or niobium (Nb) in amount considering the electrovalence balance and ionic radii.

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CONCLUSION

By means of mixed oxide method and pressureless sintering in ambient atmosphere $BiNbO_4$ ceramics was fabricated. The influence of the small amount of CuO additive on microstructure and crystal structure of $BiNbO_4$ ceramic was investigated. A substantial influence of 2.5wt% of CuO on morphology of $BiNbO_4$ ceramics was found. The additive decreased porosity of ceramic samples but lots of cracks were created in the grain due to CuO evaporation. It was also found that 2.5wt% of CuO additive did not cause any change of the crystal symmetry of the $BiNbO_4$ ceramics. $BiNbO_4$ crystallized in the orthorhombic symmetry (α-$BiNbO_4$ phase, *Pnna* (52) space group). However, it was found that additive led to an increase in the elementary cell parameters and thus increases volume of the orthorhombic elementary cell.

REFERENCES

1. W. Wersing, Microwave ceramics for resonators and filters, *Current Opinion in Solid State and Materials Science* 1, 5 (1996) 715-731.
2. B. Jancar, D. Suvorov, Microwave ceramics, in: Ceramics Science and Technology, Volume 4: Applications, Edited by R. Riedel, I-W. Chen., Wiley-VCH Verlag GmbH & Co. KGaA, (2013), 321-343.
3. M.T. Sebastian, Dielectric Materials for Wireless Communications, Elsevier, Oxford, (2008)
4. Y.Ch. Liou, W.Ch. Tsai, H.M. Chen, Low-temperature synthesis of $BiNbO_4$ ceramics using reaction-sintering process, *Ceramics International* 35 (2009) 2119–2122.
5. M. Płońska, D. Czekaj, Studies of temperature and fabrication methods influence on structure and microstructure of $BiNbO_4$ microwave electroceramics, *Archives of Metallurgy and Materials* 56, 4 (2011) 1169-1175.
6. Z. Wang, X. Yao, L. Zhang, CeO_2-modified $BiNbO_4$ microwave ceramics sintered under atmosphere, *Ceramics International* 30 (2004) 1329–1333.
7. Y. Pang, Ch. Zhong, Sh. Hang, Effects of Gd doping on the sintering and microwave dielectric properties of $BiNbO_4$ ceramics, *Journal of Materials Science* 42 (2007), 7052–7055
8. D. Shihua, Y. Xi, Y. Yong, Dielectric properties of B_2O_3-doped $BiNbO_4$ ceramics, *Ceramics International* 30 (2004) 1195–1198.
9. D. Zhou, H. Wang, X. Yao, Microwave dielectric properties and co-firing of $BiNbO_4$ ceramics with CuO substitution, *Materials Chemistry and Physics* 104 (2007) 397–402.
10. L. Zhang, X. Yao, H. Wang, D. Zhou, The effect of sintering atmosphere on V_2O_5 substituted $BiNbO_4$ microwave ceramics, *Journal of Electroceramics* 21 (2008) 465–468.
11. H.R. Lee, K.H. Yoon, E.S. Kim, J.W. Choi, R. Voucher, Microwave dielectric properties of $BiNbO_4$ ceramics with CuO–V_2O_5 addition, *Ceramics International* 38S (2012) S177–S181
12. H. Kagata, T. Inoue, J. Kato, I. Kameyama, Low-fire bismuth-based dielectric ceramics for microwave use, *Japanese Journal of Applied Physics* 31 (1992) 3152–3155.
13. A. Koller (Ed.) Structure and Properties of Ceramics, Elsevier Science, 1994.
14. A. Lisinska-Czekaj, D. Czekaj, Fabrication and study of $BiNbO_4$ ceramics, *Key Engineering Materials* 512-515 (2012) 1212-1217.

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15. A. Lisinska-Czekaj, D. Czekaj, J. Plewa, Influence of processing conditions on crystal structure of $BiNbO_4$ ceramics*, Ciencia & Tecnologia dos Materiais* 29 (2017) e215-e218
16. MATCH! Version 2.0.11, CRYSTAL IMPACT, Postfach 1251, 53002 Bonn, Germany (URL: http://www.crystalimpact.com/match)
17. ISCD Database, FIZ Karlsruhe, (URL.:http://www.fiz-karlsruhe.de)
18. International Centre for Diffraction Data, 12 Campus Boulevard, Newton Square, PA 19073-3273 U.S.A.; (URL: http://www.icdd.com)
19. IUCr/COD/AMCSD Database (URL.: http://www.crystalimpact.com.match)
20. H.M. Rietveld, The Rietveld method-a historical perspective, *Australian Journal of Physics* (1988) 113-116.

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