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X-ray diffraction investigation of the defect pyrochlore $Bi_{1.61}Zn_{0.18}Ti_{1.94}V_{0.06}O_{6.62}$

V. Kahlenberg, H. Böhm

Institut für Geowissenschaften (Mineralogie), Johannes Gutenberg Universität, 55099 Mainz, Germany

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Abstract

The crystal structure of $Bi_{1.61}Zn_{0.18}Ti_{1.94}V_{0.06}O_{6.62}$ was investigated by X-ray diffraction. The compound possesses the following parameters: cubic, $a = 10.3270(10)$ Å, $V = 1101.34$ Å^3, $Z = 8$, $D_c = 6.63$ g cm^{-3}. Powder and single-crystal photographs indicate a pyrochlore-type structure. Additional weak lines in the patterns could be attributed to a slight distortion of the ideal structure in such a way that the sites occupied by Bi^{3+} belong to the 32(e) position of $Fd\bar{3}m$ and are displaced about 0.1 Å from their ideal positions in 16(c) parallel to [111]. Using a defect pyrochlore model with a substitution $Bi^{3+} \leftrightarrow Zn^{2+}$ and $Ti^{4+} \leftrightarrow V^{5+}$ a single-crystal data set could be refined down to $R_w = 0.028$.

Keywords: Pyrochlore; Defect structure; X-ray diffraction

1. Introduction

The pyrochlore structure with general formula $A_2B_2O_7$ is formed by a wide variety of ions and tolerates a high degree of non-stoichiometry on the anion and the A cation sites. The space group of the ideal pyrochlore structure is $Fd\bar{3}m$ and there are eight formula units per cell. The lattice constants vary between 10.0 Å and 10.9 Å. The bigger divalent or trivalent A cations (usually about 1.0 Å) in 16(c) (0,0,0) are eightfold coordinated and are located within a scalenohedron. The smaller B cations (about 0.6 Å) of valency +4 or +5 in 16(d) $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ are sixfold coordinated and surrounded by the anions at equal distances, forming a trigonal antiprism with an octahedron as a limiting case. The oxygen anions occupy the sites 48(f) $(x, \frac{1}{8}, \frac{1}{8})$ and 8(a) $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ respectively. These two different crystallographic oxygen anions are called O(1) and O(2). Thus in order to specify completely the three-dimensional arrangement of ions in the structure, only one positional parameter must be determined. Owing to the fact that the atoms occupy exclusively special positions, there exists a further extinction rule concerning the reflections with h, $k = 4n$, $l = 4n + 2$, in addition to the absences resulting from the symmetry operations of $Fd\bar{3}m$. Regarding the distribution of intensities in the reciprocal space, three groups of reflections can be distinguished. The weak $h,k = 4n + 2$, $l = 4n$ class depends only on the oxygen atoms. The reflections with $h, k, l = 2n + 1$ having an intermediate intensity receive contributions from all atoms but the structure factors of the A and B cations always possess an opposite sign. The A and B cations alone are responsible for the very strong reflections with Laue indices $h, k, l = 4n + 2$.

In articles on the crystal growth of Bi^{3+}-containing titanates from Bi_2O_3–V_2O_5 fluxes, a phase $Bi_2Ti_2O_7$ was reported [1]. The X-ray powder diagram of this compound was related to that of a pyrochlore structure type. The pattern was explained using an f.c.c. lattice of $a = 20.68$ Å, implying the existence of an eightfold superstructure relative to the normal pyrochlore cell. In this context it is interesting to note that this phase could only be synthesized from melts to which small amounts of ZnO were added. Without this additional component only single crystals of $Bi_4Ti_3O_{12}$, $Bi_2Ti_4O_{11}$ and TiO_2 were obtained.

The objective of the present work was to reinvestigate this pyrochlore phase because no detailed structural information is available.

2. Experimental

The single crystals investigated in this study were grown in platinum crucibles using the composition and

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temperature data given in Ref. [1]. Oxidic reagents in the molar ratio 13 mol% V_2O_5, 10 mol% ZnO, 42 mol% Bi_2O_3, and 35 mol% TiO_2 were homogenized carefully in an agate mortar. A sample of 16.5 g was placed in a 50 ml crucible on which a platinum cover was crimped. The mixture was heated from 100 °C in 11 h to 1200 °C in a resistance heated tunnel furnace; it was held at this temperature for 20 h and cooled down to 850 °C at a rate of 5 °C h^{-1}. At the end of the cooling process the melt was quenched immediately. Phase analysis of the result of the growth experiment was performed by X-ray powder diffraction. The composition of the crystals obtained was determined with a Cameca Camebax electron beam microprobe equipped with an energy-dispersive spectrometer (EDX) and four wavelength-dispersive spectrometers (WDX). The instrument was operated at 20 kV (accelerating voltage) with beam current 10 nA, using the following standards and X-ray lines for the WDX analysis: $Pb_5(VO_4)_3Cl$ (V Kα), $MnTiO_3$ (Ti Kα), $Bi_2Sn_2O_7$ (Bi Lα) and ZnS (Zn Kα). Lithium fluoride (for Bi,Zn) and pentaerythritol (for V,Ti) were used as analysing single crystals. The counting time was set at 15 s. The intensities obtained were corrected for electron scattering, absorption and fluorescence radiation (so-called ZAF correction).

All X-ray powder diffraction patterns were collected with a Seifert Iso Debyeflex 3000 θ–θ diffractometer in Bragg–Brentano geometry. Powder diffraction experiments of the pulverized single crystals were carried out using a Huber 600 Guinier camera (Cu Kα radiation, germanium monochromator). The asymmetric transmission geometry used allowed the recording of reflections with Bragg angles between 1° and 53° θ. The Guinier chamber was evacuated to reduce the background intensity due to air scattering. Silicon powder was used as an internal standard. The film data and the corrections from systematic errors (film shrinkage etc.) were evaluated using a semi-automatic Guinier film reader in combination with the program Jagokor [2]. The corrected line positions were used to refine the cell parameter by the least squares method with the program LCC [3].

Table 1
Parameters for the X-ray data collection

Temperature (°C)	23°C
Space group	$Fd\bar{3}m$
a (Å)	10.3270(10)
V (Å^3)	1101.34
h, k, l limits	1/12; 0/8; 0/7 ($l \geqslant 0$, $k \geqslant 1$, $h \geqslant k$)
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.594
Measured reflections	74
Observed reflections ($I > 2\sigma(I)$)	68

For the single-crystal investigations, specimens of good optical quality were selected and ground to spheres. The reflection-shapes screened by Laue photographs taken before and after the grinding process revealed a distinct broadening for some samples. A crystal sphere (radius 0.042 mm) without any indications of broadening effects was chosen for further structural examinations. Photographs of different layers of the reciprocal lattice were taken by a Seifert precession camera (Mo Kα radiation) equipped with a graphite monochromator.

Data collection for the crystal structure analysis was carried out with an Enraf-Nonius CAD-4 four circle diffractometer with graphite monochromated Mo Kα radiation in ω–2θ step scan mode (Table 1). The setting angles of 18 reflections were used for determination and refinement of the lattice parameters. The intensity and orientation of three standard reflections were monitored regularly. Data reduction including Lorentz polarization and spherical absorption corrections ($\mu R = 2.20$) was accomplished using the program system MolEN [4]. Other computer programs used in the course of this investigations were SHElX76 [5] for structure refinement and SADIAn91 [6] for determination of interatomic distances and angles. Atomic scattering factors and real and imaginary anomalous-dispersion coefficients were taken from Ref. [7]. The refinements were calculated by the full-matrix least squares method minimizing the function $\Sigma\omega(|F_o| - |F_c|)^2$ ($\omega = 1/\sigma(F)^2$). No extinction correction was applied.

3. Results

The diffraction pattern used for identification of the phases of the entire batch is given in Fig. 1. Only two

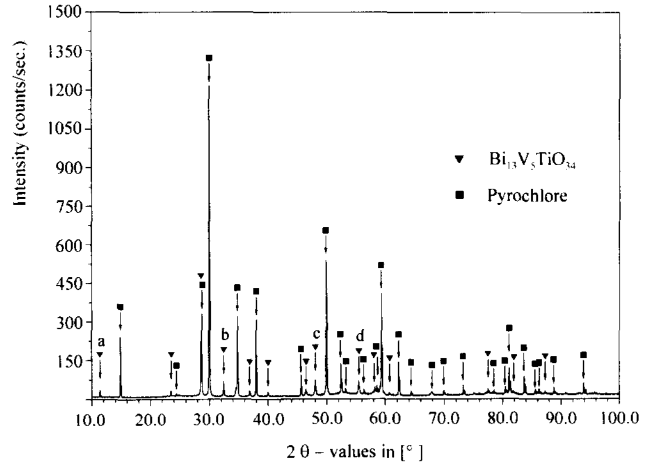

Fig. 1. X-ray powder diffraction pattern of the products of the whole single-crystal synthesis including the solidified flux; lines (a)–(d) correspond to the lattice planes with d values of 7.8 Å, 2.77 Å, 1.892 Å and 1.658 Å respectively which were used in [1] for the postulation of an eightfold superstructure.

phases were ascertained: $Bi_{13}V_5TiO_{34}$ (PDF 36-235) building up a microcrystalline matrix and large crystals of a pyrochlore-type phase of amber-like colour. The crystals were leached from the matrix of solidified flux with warm 3 molar nitric acid. The samples obtained showed external faces of the {111} form having edges up to 5 mm in length and habits ranging from regular-looking octahedra to tabular shapes with a hexagonal or triangular-like outline. A first qualitative analysis of these crystals using an EDX spectrum revealed the incorporation of small amounts of Zn and V as well as major quantities of Bi and Ti. The final analysis was accomplished using a WDX spectrometer. The superposition of the V Kα line employed for determination of the V content with the Ti Kα line was accounted for by measuring the apparent V content in a V-free Ti standard. The analysis yielded to a composition of 27.24 mol% Bi_2O_3, 65.62 mol% TiO_2, 1.03 mol% V_2O_5, and 6.12 mol% ZnO.

For calculation of a pyrochlore formula from the oxidic components, substitution of Bi^{3+} by Zn^{2+} (as described in [8] for pyrochlore-type ruthenates) and of Ti^{4+} by V^{5+} was assumed. Using this approach the formula $Bi_{1.61}Zn_{0.18}Ti_{1.94}V_{0.06}O_{6.62}$ was derived. Therefore the actual compound is a defect pyrochlore where the positive charge deficiency at the A site is compensated primarily through defects at the oxygen positions.

As a first step in structural characterization a Guinier film photograph of several isolated and powdered single crystals was taken. All lines could be indexed with an f.c.c. unit cell of 10.3300(3) Å (see Table 2). The distribution of the intensities among the different groups of reflections seems to confirm the assumption of a pyrochlore structure type, but some of the weak lines are of special interest. The (842) reflection violates the pyrochlore specific extinction rule of the class with $h, k=4n, l=4n+2$. The reflections at $\theta_1=53.145°$ and $\theta_2=75.890°$ can be indexed using the Laue indices (442) and (644) or (600) and (820). In the first case these two lines belong to the same group as the (842) reflection. They indicate a slight modification of the ideal pyrochlore structure but are still in agreement with the general extinction rules of $Fd\bar{3}m$. Using the second indexing possibility these lines would implicate a structural deviation from the ideal pyrochlore model, resulting in a reduction in space group symmetry because ($hk0$) reflections with $h+k\neq 4n$ are not allowed by symmetry in $Fd\bar{3}m$.

In order to settle this point, precession photographs of layers perpendicular to the [100] and [110] directions respectively were taken. On over-exposed pictures weak (442) and (644) reflections were clearly visible. There was no evidence of symmetry forbidden reflections.

According to the results of the previous sections the structure determination was started using a defect pyrochlore model in space group $Fd\bar{3}m$ (origin at $\bar{3}m$) with the Bi^{3+} and Zn^{2+} cations disordered on the A site at 32(e) (x,x,x). The Ti^{4+} and V^{5+} cations were distributed statistically at 16(d). The site occupation factors were not refined but kept fixed to the values resulting from the chemical analysis. The isotropic temperature factors of the cations on the mixed A and B sites were constrained to be equal.

The refinement based on this approach converged to a final weighted residual of $R_w=0.028$ for all reflections with $I\geqslant 2\sigma_I$ and six variable parameters. Table 3 contains the coordinates, temperature coefficients and occupation factors. The (Bi,Zn) ions are surrounded by eight O atoms: two O(2) anions with distances of 2.134(3) Å and 2.337(3) Å and six O(1) anions in 48(f) (3×2.535(7) Å and 3×2.571(7) Å). The (Ti,V) cations are coordinated octahedrally. The distance from the central cation to the six O(1) is 1.993(6) Å. Neglecting the V content on the site, this value for the bond lengths is within the range known for TiO_6 octahedra in many other compounds [9]. In this case the octahedron is not regular but the x(O(1)) parameter influencing the shape of the coordination figure of the Ti atom is close to 7/16 = 0.4375 for an ideal form. The distortion is reflected in the O(1)–Ti–O(1) angles of 95.76(3)° (×6) and 84.24(2)° (×6) deviating from 90°, whereas the third angle is 180°.

The cations on the A position are displaced about 0.1 Å parallel to the [111] direction towards the partly occupied oxygen position at 8(a). Within this model a distinction between the displacements of Bi^{3+} and Zn^{2+} cannot be accounted for, but from the lone-pair electron character of the Bi^{3+} one can infer that only the trivalent bismuth is involved in the distortion.

4. Discussion

The results of our investigations disagree with the data published in [1] with regard to the chemical composition of the crystals. The amount of Bi^{3+} and Ti^{4+} in the work of these authors was determined by wet chemical analysis. Possible contents of Zn^{2+} and V^{5+} were not accounted for. In particular, by ignoring the ZnO component which obviously induced the crystallization of this phase, the published results become questionable. Neither our powder nor our single-crystal X-ray diffraction patterns revealed any evidence for a face-centred superstructure of 20.68 Å. A close inspection of the PDF entry 32-118 based on the data of [1] shows that the enlargement of the cell is inferred from five lines. Taking the comment on this card into consideration, that the first line was originally given by the authors as 7.8 Å four of these reflections can

Table 2
Results of the evaluation of a Guinier film ($\lambda = 1.54056$ Å), figures of merit, $M_{20} = 151$, $F_{29} = 96$, $\langle|\Delta 2\theta|\rangle = 0.0097$, $N_{poss} = 31$

Number	*hkl*	$2\theta_{obs}$	$2\theta_{calc}$	d_{obs}	d_{calc}	I_{rel}
1	(111)	14.833	14.841	5.964	5.967	40
2	(220)	24.330	24.351	3.652	3.655	1
3	(311)	28.643	28.637	3.115	3.114	20
4	(222)	29.946	29.939	2.982	2.981	100
5	(400)	34.709	34.707	2.582	2.582	20
6	(331)	37.940	37.935	2.370	2.369	30
7	(422)	42.826	42.852	2.108	2.110	1
8	(333), (511)	45.594	45.593	1.9880	1.9880	10
9	(440)	49.912	49.898	1.8261	1.8256	40
10	(531)	52.363	52.354	1.7461	1.7458	10
11	(442), (600)	53.145	53.154	1.7217	1.7220	1
12	(620)	56.280	56.277	1.6333	1.6332	1
13	(533)	58.562	58.546	1.5753	1.5749	1
14	(622)	59.299	59.289	1.5573	1.5571	30
15	(444)	62.218	62.211	1.4910	1.4909	40
16	(551), (711)	64.350	64.351	1.4465	1.4465	1
17	(642)	67.843	67.836	1.3804	1.3803	1
18	(553), (731)	69.852	69.886	1.3449	1.3454	1
19	(800)	73.245	73.244	1.2913	1.2912	5
20	(644), (820)	75.890	75.888	1.2527	1.2527	1
21	(660), (822)	78.486	78.502	1.2174	1.2176	1
22	(555), (751)	80.443	80.447	1.1928	1.1929	10
23	(662)	81.096	81.092	1.1849	1.1849	40
24	(840)	83.667	83.664	1.1549	1.1549	30
25	(911), (753)	85.570	85.584	1.1339	1.1340	10
26	(842)	86.243	86.222	1.1271	1.1269	1
27	(664)	88.779	88.774	1.1012	1.1011	1
28	(844)	93.860	93.874	1.0543	1.0544	20
29	(933), (755)	95.805	95.792	1.0382	1.0381	10

Table 3
Fractional atomic coordinates and isotropic temperature factors

		Site	*x*/*a*	*y*/*b*	*z*/*c*	Occupation factor	*U*(Å^2)
Bi	A	32(e)	0.0057(3)	0.0057(3)	0.0057(3)	0.0672	0.0100(4)
Zn						0.0075	
Ti	B	16(d)	0.5000	0.5000	0.5000	0.0808	0.0058(9)
V						0.0025	
O(1)		48(f)	0.4226(9)	0.1250	0.1250	0.2500	0.0117(23)
O(2)		(8a)	0.1250	0.1250	0.1250	0.0260	0.0397(61)

be attributed to the compound $Bi_{13}V_5TiO_{34}$. A comparison with the data of Fig. 1 shows that these lines also occur in the powder pattern of the sample of the entire batch. Therefore we conclude that the "superlattice reflections" are likely to arise from an impurity.

A coupling between the existence of a defect pyrochlore structure and a displacement of the ion occupying the A site parallel to [111] has been described more than once in the literature. Many of these $A_2B_2O_{7-x}$-type oxides have weakly basic ions such as Tl^+, Pb^{2+}, Bi^{3+} with an easily polarizable $6s^2$ lone pair of electrons as the A cation. $Pb_2Ru_2O_{6.5}$ [10] and $Pb_2TiSbO_{6.5}$ [11] can be considered as examples of this kind of structure. In both cases the displacement from the position in 16(c) is about 0.04 Å. The X-ray and neutron diffraction pattern of these compounds also showed additional weak reflections, but in contrast to the phase discussed in this publication, these lines violated the extinction rules of $Fd\bar{3}m$ for the ($hk0$) and ($h00$) classes. A structural model was found in the space group $F\bar{4}3m$. The displacement of the Pb^{2+} ions was the result of an ordering process between the oxygen anions and the vacancies at the 8(a) position. The distortion towards the ordered vacancies initiated a loss of centrosymmetry. A further symmetry reduction to the tetragonal space group $P\bar{4}2m$ was reported for $PbTlNb_2O_{6.5}$ where additional ordering of the Pb and Tl ions occurred [10]. The occupation of the 32(e) position without any change in the space group symmetry of $Fd\bar{3}m$ was first noted in Ref. [12] for Tl^+ in the inverse pyrochlore $Tl_{0.77}H_{0.63}(H_2O)_y(Nb_{1.40}W_{0.60})O_6$.

$Bi_{1.61}Zn_{0.18}Ti_{1.94}V_{0.06}O_{6.62}$ has an intermediate position in the group of defect pyrochlores between members with an unmodified pyrochlore structure such as $Bi_2Rh_2O_{6.8}$ [13] or $Bi_{1.7}Cu_{0.2}Ti_2O_{6.8}$ [14] on one side and the above-mentioned examples indicating a reduction in space group symmetry. Bi^{3+} is displaced from its ideal position at 16(c) but the distortion is distributed randomly over the possible [111] directions and not correlated with any ordering process of the anion vacancies in 8(a).

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References

[1] S. Shimada, K. Kodaira and T. Matsushita, *J. Cryst. Growth, 41* (1977) 317–320.

[2] H. Kroll, D. Stöckelmann and A. Zingel, JAGOKOR, Programm zur Auswertung und Korrektur von Röntgen-Pulverfilmen, Universität Münster, Germany, 1990.

[3] C.W. Barnham, *LCC*, Geophysical Laboratory, Carnegie Institution of Washington, 1963.

[4] Enraf-Nonius, *MolEN*, An interactive intelligent system for crystal structure analysis, Delft, 1990.

[5] G.M. Sheldrick, SHELX76, Program for crystal structure determination, University of Cambridge, 1976.

[6] W.H. Baur, G. Wenninger, S.D. Roy and D. Kassner, SADIAN91, Universität Frankfurt, 1986.

[7] J.A. Ibers and W.C. Hamilton, *International Tables for X-Ray Crystallography*, Vols. I–IV, Kynoch Press, Birmingham, 1974.

[8] M. Schuler and S. Kemmler-Sack, *J. Less-Common Met., 102* (1984) 105.

[9] E. Tillmanns, W. Hofmeister and W.H. Baur, *J. Solid State Chem., 58* (1985) 14–28.

[10] Beyerlein *et al.* (1984), *J. Solid State Chem., 51* (1984) 253–265.

[11] J.A. Alonso, C. Casclaes, I. Rasines and J. Pannetier, *Acta Crystallogr. C, 45* (1989) 3–7.

[12] M. Gasperin, *Mater. Res. Bull., 9* (1974) 1053–1056.

[13] J.P. Longo, P.M. Raccah, J.A. Kafalas and J.W. Pierce, *NBS Special Publ., 364* (1972) 219–226.

[14] I. Bryntse, *Eur. J. Solid State Inorg. Chem., 28* (1991) 481–492.