Structural Studies of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ Solid Solutions ($0.1 \leq x \leq 1.0$) Prepared by a Combined Mechanochemical/Thermal Synthesis

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Structural Studies of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ Solid Solutions ($0.1 \leq x \leq 1.0$) Prepared by a Combined Mechanochemical/Thermal Synthesis

Dedicated to Professor Rüdiger Kniep on the occasion of his 65th birthday

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Abstract

$\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions with $0.1 \leq x \leq 1.0$ prepared via mechanochemical processing of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ mixtures and subsequent annealing have been investigated by X-ray diffraction, Mössbauer spectroscopy, and EDX. A Rietveld refinement was made for the whole range of the solid solutions. The structure is orthorhombic with space group *Pbam*. Mössbauer spectroscopy reveals paramagnetic behaviour for $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ with $0.1 \leq x \leq 1.0$ at room temperature and indicates significant distortion of the octahedral iron coordination for aluminium-rich mixed crystals. The occupancy of octahedrally and tetrahedrally coordinated sites was determined by Mössbauer spectroscopy and Rietveld analysis. For $x \geq 0.5$, the Mössbauer measurements as well as the Rietveld refinements show an almost random distribution of aluminium and iron cations over the two non-equivalent sites, whereas for $x < 0.5$ a slight preference of iron for the octahedral sites is observed.

Keywords: mullite-type compounds, Mössbauer spectroscopy, Rietveld, cation distribution, $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$

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Introduction

Bismuth-bearing oxides $\text{Bi}_2\text{M}_4\text{O}_9$ ($\text{M} = \text{Fe}^{3+}$, Ga^{3+} , Al^{3+} and In^{3+}), their substituted derivatives $\text{Bi}_{2-2x}\text{A}_{2x}\text{M}_4\text{O}_{9-x}$ (e.g. $\text{A} = \text{Sr}^{2+}$, $\text{M} = \text{Al}^{3+}$, Ga^{3+} , Fe^{3+}), and the wide variety of respective solid solutions are members of the mullite-type family of crystal structures [1-5]. These compounds are orthorhombic and crystallize in the space group *Pbam*. The structure is characterized by columns of edge-sharing MO_6 octahedra parallel to the c-axis which are interconnected by M_2O_7 double tetrahedra, Fig. 1. The octahedral and tetrahedral sites occur in equal numbers. Because columns of edge-sharing octahedra around M^{3+} ions constitute the characteristic feature of the mullite structure, compounds of the $\text{Bi}_2\text{M}_4\text{O}_9$ family are termed mullite-type compounds [1].

In mullite-type bismuth metal oxides, the two non-equivalent sites for M^{3+} ions can accept both transition and main group metal ions and, therefore, many materials properties depend on the distribution of the different M^{3+} cations on the two non-equivalent sites. Some of these materials show remarkable ionic conductivity of anions [5,6] having potential as electrolytes in solid oxide fuel cells (SOFC) or as oxygen sensors [7,8]. Others possess a high emissivity in the infra red region and, thus, may be utilized as high energy scintillator materials [9,10]. Recent interest in $\text{Bi}_2\text{Fe}_4\text{O}_9$ has also focused on its photocatalytic activity [11,12] and on its gas sensing [13,14], dielectric [15], electronic [16], magnetic [17], and multiferroic [18] properties. Another point of fundamental interest in these materials is related with the role played by the lone electron pair of Bi^{3+} ions in respect to structure and materials properties of this class of compounds [2].

Various methods have been described for the synthesis of polycrystalline $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions. Giaquinta et al. [4] have annealed stoichiometric amounts of oxides at 850°C in air for two weeks with frequent grindings. More recently, Voll et al. [19] applied the glycerine method for the synthesis of mixed crystals using temperatures up to 850°C. Pure [6] and doped [5] $\text{Bi}_2\text{Al}_4\text{O}_9$ have been prepared by the combustion synthesis route using the glycine-nitrate process and followed by high-temperature sintering at 1050-1090°C. In another powder synthesis of $\text{Bi}_2\text{Al}_4\text{O}_9$ annealing temperatures of 1000°C have been used [20]. $\text{Bi}_2\text{Fe}_4\text{O}_9$, the iron end member of the solid solution, has been prepared from the powders at temperatures ranging from 850°C to 950°C [7,14,21]. In the present work, the synthesis of mullite structure type $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions with $0.1 \leq x \leq 1.0$ via mechanochemical processing of stoichiometric $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ mixtures and subsequent annealing is

reported. Compared to the above mentioned conventional (thermal) routes, the combined mechanochemical/thermal process used here represents a simple, high-yield, lower temperature, shorter processing time, and, thus, a low-cost procedure for the synthesis of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$.

In the present contribution, we explore the local structural properties of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions by a combined X-ray diffraction and ^{57}Fe Mössbauer spectroscopy study. On the basis of Rietveld analysis of the XRD data, the coordinates of atoms, the unit cell dimensions, and the atom occupation factors in the investigated systems are determined. In parallel, quantitative information on the iron site occupancy in the mixed crystals and on local structure is obtained from Mössbauer spectroscopy. In this context, the paper also addresses the question of how the four experimentally observed quadrupole transitions of almost equal intensity can be assigned to the two different structural sites for iron in the mullite-type structure of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$.

Experimental Section

Polycrystalline $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions in the range $0.1 \leq x \leq 1.0$ were prepared from mixtures of Bi_2O_3 (Alfa Aesar, 99.999%), $\alpha\text{-Fe}_2\text{O}_3$ (Alfa Aesar, 99.998%), and $\alpha\text{-Al}_2\text{O}_3$ (Aldrich, 99.998%) by a combined mechanochemical/thermal synthesis method using a high-energy planetary ball mill (Pulverisette 6, Fritsch). The starting materials were weighed in stoichiometric amounts and milled in a chamber (250 cm^3 in volume) with 22 balls (10 mm in diameter) both made of tungsten carbide. The powders were milled for 3 hours at 600 rpm with a ball-to-powder weight ratio of 22:1. After this procedure, the as-milled materials were annealed at 800°C in air for 24 hours.

Figure 2 displays a representative EDX spectrum of the solid solution $\text{Bi}_2\text{Fe}_2\text{Al}_2\text{O}_9$. It shows only the peaks corresponding to the constituent elements of Bi, Fe, Al, and O and indicates that there is no contamination from the tungsten carbide chamber and balls used in the mechanochemical treatment. In addition, the average atomic concentrations of Bi (14.7 at%), Fe (14.5 at%), Al (16.0 at%), and O (54.8 at%) (estimated error $\pm 1\%$) are found to be in good agreement with the stoichiometric formula. Note, however, that the oxygen atomic percentage is not so well reproduced since oxygen is a light atom.

The XRD data of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ ($0.1 \leq x \leq 1$) mixed crystals were collected using a PW 1820 X-ray diffractometer (Philips, Netherlands), operating in Bragg configuration and using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$). X-ray powder diffraction step scans were taken from 10° to $80^\circ 2\theta$, using a step size of $0.02 2\theta$ and a data collection time of 5 sec/step. The Rietveld refinements of the XRD data were performed using a full-profile analysis program [22].

^{57}Fe Mössbauer spectroscopic measurements were carried out in transmission mode at room temperature. ^{57}Co in Rh was used as γ -ray source. For the quantitative analysis of the Mössbauer spectra the *Recoil* spectral analysis software was employed [23].

Results and Discussion

X-ray diffraction patterns of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions prepared by the mechanochemical/thermal synthesis and a representative Rietveld refinement of the XRD data for the solid solution with $x = 0.5$ are shown in Figs. 3 and 4. All the diffraction peaks correspond to the orthorhombic mullite-type phase with space group *Pbam*, thus showing no evidence of secondary phases. In particular, no traces of the perovskite-type BiFeO_3 phase were observed. Therefore, the combined mechanochemical/thermal preparation process (high-energy milling of the reaction educts for 3 h followed by annealing at 800°C for 24 h) results in a pure $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solution for $0.1 \leq x \leq 1.0$. It should be noted that conventional (thermal) preparation routes to $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions requires a prolonged heat treatment, see e.g. [4], and/or considerably higher temperatures as, e.g., in Ref. [20]. In Fig. 4, the solid curve represents the fit according to the refinement. The full circles are the observed X-ray diffraction data and at the bottom, the difference between observed and calculated intensities is shown (lower continued line). Information on the Rietveld refinement of Fig. 4, crystallographic data, and *R*-values are listed in Table 1. The Rietveld analysis reveals that iron and aluminum are almost statistically distributed over the cation sites of octahedral and tetrahedral coordination. However, the refinements for samples with lower iron concentrations show that Fe ions develop a slight preference for the octahedral sites for $x < 0.5$ with an occupancy around 55%, see Table 3 and Fig. 9 below. The lattice parameters of the $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solution with $0.1 \leq x \leq 1.0$ are shown in Fig. 5. They increase with increasing iron concentration, as expected according to Vegard's law.

Room temperature ^{57}Fe Mössbauer spectra of the as-prepared $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions are shown in Fig. 6. Spectra of all samples reveal paramagnetic behaviour for $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ with $0.1 \leq x \leq 1.0$. The experimental spectra consist of four quadrupole transition. They were least-squares fitted by resonance signals for the octahedral and the tetrahedral sites, where each sub-spectrum is split into a doublet structure by electric quadrupole interactions. Due to their isomer shifts (with reference to $\alpha\text{-Fe}$ at 290 K) of about 0.2 mm/s and 0.3 mm/s, the subspectra can be attributed to tetrahedrally (light gray) and octahedrally (dark gray) coordinated Fe^{3+} ions, respectively [24]. The fitted hyperfine parameters are listed in Table 2. The present assignment of the quadrupole doublets and of the spectral parameters are in agreement with literature data for $\text{Bi}_2\text{Fe}_4\text{O}_9$ [21,25-28]. It is to be noted, however, that the assignment of the transitions is not unique in the present case involving four transition of almost equal intensity. We have adopted here the fit strategy using one inner and one outer doublet introduced by Bokov et al. [25] and later used by almost all other authors, see Refs. [21,26-28], with the notable exception of Giaquinta et al. [4] who used two overlapping doublets. This discussion will be taken up again and continued below. To the best of our knowledge, the only attempt in the literature to validate the ad-hoc assignment by Bokov et al. [25] has been undertaken by Kostiner and Shoemaker [21] by substituting a portion of the iron ions by chromium and assuming that chromium ions are mainly located on the octahedrally coordinated sites.

The analysis of Mössbauer spectra of the $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ mixed crystals reveals that isomer shifts of the two spectral components are linearly dependent on the iron content, see Fig. 7. The observed decreases of IS_O and IS_T by about 0.03 mm/s with decreasing iron content are due to an increase of s-electron density at the Fe nuclei in both sites. This goes in parallel with the shrinking of lattice volume as derived from XRD, see Fig. 5. Thus, the observed increase of s-electron density at the ^{57}Fe nuclei can be interpreted as being due to an increasing lattice pressure on Fe with increasing aluminium content. On the other hand, as has been pointed out by Menil [24], the inductive effect of a competing $\text{M}^{3+}\text{-O}$ bond on the covalency of the $\text{Fe}^{3+}\text{-O}$ bond may also result in decreasing iron isomer shifts if the M^{3+} ions possess a smaller electronegativity, χ , than Fe^{3+} . In the present case, indeed $\chi(\text{Al}^{3+}) < \chi(\text{Fe}^{3+})$ holds, see e.g. [29], and, thus, this inductive effect can also explain the observed shift variation brought about by the increasing number of aluminium-oxygen bonds in the aluminium-rich mixed crystals.

Figure 8 shows the quadrupole splittings, QS_O and QS_T , of the two subspectra. The quadrupole splittings at both sites increase monotonously with the increasing aluminium content of the mixed crystals. This indicates that the addition of Al^{3+} brings about a general contraction of the lattice, see Fig. 5, resulting in larger electric field gradients and consequently larger quadrupole splittings. Based on simple point charge interactions and almost isotropic volume change of the lattice, quadrupolar interactions are expected to vary as r^{-3} , where $r^2 = a^2 + b^2 + c^2$ and where a, b, and c are the orthorhombic lattice parameters. However, the two structural sites are very differently affected by the increasing aluminium content: while the quadrupole splitting of tetrahedral sites increases by about 9% with x decreasing from x=1.0 to x=0.1, the splitting at octahedral sites increases by about 40%. Thus, the almost linear variation observed for the tetrahedrally coordinated sites is in good agreement with the qualitative expectations in the framework of the simple model indicated above which predicts an increase of QS by 11%. The splitting at the octahedral sites, however, does not agree with expectations and in addition exhibits a significantly non-linear dependence on composition. Therefore, one is led to conclude that the octahedral site, in addition to the general lattice contraction, undergoes a significant distortion upon the introduction of aluminium ions into the structure resulting in an enhanced electric field gradient and larger quadrupole splitting for this site.

The ^{57}Fe Mössbauer spectra have also been evaluated in respect to the distribution of iron on tetrahedrally and octahedrally coordinated sites. The area (A_i) ratio of the two respective subspectra is given by

$$\frac{A_T}{A_O} = \frac{G_T \Gamma_T N(Fe_T) f_T(x)}{G_O \Gamma_O N(Fe_O) f_O(x)}$$

Here, G_i are saturation factors and Γ_i represent the line widths of the subspectra. $N(Fe_i)$ denote the number of iron ions per formula unit in the indicated site and $f_i(x)$ are the corresponding Debye-Waller factors. Whereas the saturation factors and line widths can be safely assumed identical for both subspectra, the Debye-Waller factors of both structural sites as well as their possible dependences on composition of the mixed crystals are unknown. As an approximation, it will therefore be assumed that the ratio of the recoil-free fractions, f_T/f_O , of the two sites is independent of the chemical composition of the sample, i.e. it is assumed that $f_T(x)/f_O(x) = f_T(x=1)/f_O(x=1)$. The latter ratio can be determined from the pure iron end member $Bi_2Fe_4O_9$ of the solid solution series where the iron ions are occupying octahedral

and tetrahedral sites in equal numbers, $N(\text{Fe}_\text{O}) = N(\text{Fe}_\text{T}) = 2$. The Debye-Waller factor ratio of ferric ions in $\text{Bi}_2\text{Fe}_4\text{O}_9$ ($x = 1$) at room temperature has been determined as $f_\text{T}/f_\text{O} = 1.045$ from the measured areas A_T and A_O , see Table 3. This value was used for the calculation of the iron distribution between T and O sites in the series of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ samples with x ranging from 0.1 to 0.9, see Fig. 9. It is interesting to note that a very similar value of 1.064 was obtained for the f_T/f_O ratio in a study of the spinel Fe_3O_4 [30]. Thus, the present approximation appears very appropriate.

The results obtained from Mössbauer spectroscopy on site-populations are in good agreement with those derived from the Rietveld refinements. In particular, the Mössbauer data show the same deviation from the random distribution of iron and aluminium ions for $x < 0.5$, whereas the distribution is almost random for $x \geq 0.5$. The cation distributions obtained from the two experimental methods are compared in Fig. 9. The present finding for $x < 0.5$ represents an extension of the previous knowledge on the cation distribution in $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ mixed crystals. Following Giaquinta et al. [4], this distribution in the previous literature is considered to be random. However, these authors only studied mixed crystals with $x \geq 0.5$ and, thus, missed the change in the cation distribution of the aluminium-rich solid solutions where aluminium is found to develop a slight, but definite preference for the tetrahedral coordination.

A comment is in order in respect to the thermodynamics of the cation distribution because the close to random distribution observed for the whole $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solution series may appear unexpected in view of the different sizes of Fe^{3+} (0.79 Å) and Al^{3+} (0.68 Å) [31]. After the mechanochemical step in sample preparation, the samples are still of multi-phase nature. After the 24 hours of annealing, samples are cooled down rapidly and, thus, cation distributions observed at room temperature may correspond to a distribution at 800°C or slightly lower temperatures. In order to ascertain that the observed distributions represent real equilibrium states, we have generated non-equilibrium distributions in our as prepared samples and followed their relaxation into equilibrium. For this, e.g. a sample with $x = 0.5$ possessing a site population ratio of $N(\text{Fe}_\text{O})/N(\text{Fe}_\text{T}) \approx 1.04$, see Fig. 9, has been milled in a high-energy ball mill for 1 hour. After that, according to its Mössbauer spectrum, the sample is still single phase with, however, a significantly reduced concentration of iron ions on octahedral sites with an iron site population ratio of $N(\text{Fe}_\text{O})/N(\text{Fe}_\text{T}) \approx 0.45$, Fig. 10a. After 0.5 h of annealing at 800°C, the sample shows virtually the same cation distribution and spectral

parameters, Fig. 10b, as initially observed, see Fig. 6 and Table 3. This finding indicates a remarkably short relaxation time of the cation distribution of probably less than 10 min. Further on, it provides strong evidence for the fact that the cation distributions studied in the present work represent true equilibrium cation distributions.

The spectrum of the mechanically treated material, Fig. 10a, exhibits a significantly increased quadrupolar splitting of the octahedrally coordinated iron species if compared with the equilibrium material with $x = 0.50$, Fig. 6 and Table 2, and with the re-equilibrated material, Fig. 10b. The splitting takes a value of about 0.55 mm/s which is to be compared with a splitting of about 0.50 mm/s for the other materials. This value of 0.55 mm/s is close to the maximum values observed for QS_O for small iron contents of the equilibrium material, see Fig. 8. Thus, it appears that the enrichment of aluminium ions in the columns of the octahedral sites is associated with and reason for the distortion of the octahedral iron coordination at low iron content causing the increasing quadrupolar interactions at these sites with decreasing iron content. Obviously, the population of the tetrahedral sites exerts no significant influence on the quadrupolar interaction at octahedral sites.

A final comment in relation to Fig. 10a is concerned with the assignment of sites and the fitting strategy chosen in the present work. The non-equilibrium cation distribution reached in the mechanically treated material represents the most divergent concentrations of iron on the two sublattices that have been reported for the $Bi_2(Fe_xAl_{1-x})_4O_9$ system and, thus, is of even higher significance in the present context than the substitution strategy used by Kostiner and Shoemaker [21] where about 6% of total iron were replaced by chromium resulting in an experimental area ratio of $A_O/A_T \approx 0.88$. In the our case, the goodness of fit criterion, χ^2 , for Fig. 10a takes a value of 1.25 for the present fit strategy using one inner doublet for octahedral sites and one outer doublet for tetrahedral sites. In comparison, a fit using two overlapping doublets yields $\chi^2 = 1.80$. In conclusion, the by far superior quality of fit obtained in the first case provides a strong argument for the validity of the fit strategy adopted in the present paper. It must be admitted, however, that the χ^2 -value of 1.25 for the mechanically treated material is significantly larger than the ones usually observed in our fits which consistently were found to take values close to 1.0 (e.g., $\chi^2=1.003$ for Fig. 10b). This may be due to the action of the high-energy milling process which leads to the fragmentation of the sample material causing the formation of a certain fraction of particles in the nano meter range. This process is associated with the formation of iron species experiencing new

environments, e.g., at the boundaries of the nano crystallites and thus can lead to the formation of new components in the Mössbauer spectra which were not accounted for in the fits.

Conclusions

Mullite-type $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions with $0.1 \leq x \leq 1.0$ have been synthesized via high-energy ball milling of $\alpha\text{-Fe}_2\text{O}_3/\text{Bi}_2\text{O}_3/\text{Al}_2\text{O}_3$ mixtures followed by subsequent annealing at 800°C for 24 hours. Obviously, mechanical preactivation of the reaction precursors enhances their reactivity in the syntheses of the mixed crystals, thus decreasing both the reaction temperature and time of the subsequent thermal process. Compared to alternative chemical routes, the process used here represents a simple, high-yield, lower temperature, and faster procedure for the synthesis of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ mixed crystals.

Samples have been investigated by XRD and ^{57}Fe Mössbauer spectroscopy. The Rietveld refinements of the mixed crystals reveal a slight preference of Fe^{3+} for the octahedral site for $x < 0.5$, whereas for $x \geq 0.5$, the solid solutions possess an almost random distribution of iron and aluminium ions on the octahedrally and tetrahedrally coordinated sites of the structure. Lattice parameters of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ mixed crystals vary linearly with iron content and change in accordance with Vegard's law.

The ^{57}Fe Mössbauer spectra of all samples of the $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ series can be fitted by two paramagnetic quadrupole-split subspectra due to Fe^{3+} ions in sites of tetrahedral and octahedral coordination. The Mössbauer isomer shifts IS_O and IS_T reflect an increase of s-electron density at the ^{57}Fe nuclei with decreasing iron content x . The quadrupole splittings of both sites increase with Al concentration which is in parallel with the general contraction of the lattice as derived from XRD, resulting in larger electric field gradients. In the case of the tetrahedral site, the observed increase by about 10% correlates very well with the variation expected for the lattice contribution to electric field gradients in the framework of a simple point charge model and almost isotropic lattice expansion. In the case of the octahedral site, however, the observed increase of the quadrupolar interaction of about 40% is not compatible with such a simple model. This discrepancy leads to the conclusion that the coordination of the iron-occupied octahedral site is increasingly distorted as the aluminium content of the mixed crystals increases. Finally, excellent agreement has been found for site occupancies as

derived from Mössbauer spectroscopy and the Rietveld refinements. In particular, the slight preference of Fe^{3+} for the octahedral site for $x < 0.5$ is also observed by Mössbauer spectroscopy. In this context, the confirmation of validity of the fit strategy of the Mössbauer spectra adopted in the present paper represents an important aspect of the present work.

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References

- [1] R.X. Fischer, H. Schneider, in *Mullite*, ed. H. Schneider, S. Komarneni, Wiley-VCH, Weinheim **2005**, p. 1.
- [2] J. Schreuer, M. Burianek, M. Mühlberg, B. Winkler, D.J. Wilson, H. Schneider, *J. Phys.: Condens. Matter* **2006**, 18, 10977.
- [3] D.M. Giaquinta, G.C. Papaefthymiou, W.M. Davis, H.-C. zur Loye, *J. Solid State Chem.* **1992**, 99, 120.
- [4] D.M. Giaquinta, G.C. Papaefthymiou, H.-C. zur Loye, *J. Solid State Chem.* **1995**, 114, 199.
- [5] S. Zha, Cheng, Y. Liu, X. Liu, G. Meng, *Solid State Ionics* **2003**, 156, 197.
- [6] I. Bloom, M.C. Hash, J.P. Zebrowski, K.M. Myles, M. Krumpelt, *Solid State Ionics* **1992**, 53-56, 739.
- [7] I. Abrahams, A.J. Bush, G.E. Hawkes, T. Nunes, *J. Solid State Chem.* **1999**, 147, 631.
- [8] J.B. Goodenough, *Ann. Rev. Mater. Res.* **2003**, 33, 91.
- [9] G. Blasse, O. Boen, *J. Luminesc.* **1980**, 21, 165.
- [10] V.V. Volkov, A.V. Egorysheva, *Opt. Mater.* **1996**, 5, 273.
- [11] Q.-J. Ruan, W.-D. Zhang, *J. Phys. Chem. C* **2009**, 113, 4168.
- [12] N.I. Zakharchenko, *Kinetics and Catalysis* **2002**, 43, 95.
- [13] Q.-J. Ruan, W.-D. Zhang, *Mater. Lett.* **2008**, 62, 4303.
- [14] A.S. Poghossian, H.V. Abovian, P.B. Avakian, S.H. Mkrtchian, V.M. Haroutunian, *Sensors and Actuators B* **1991**, 4, 545.
- [15] Y.A. Park, K.M. Song, N. Hur, *J. Korean Phys. Soc.* **2008**, 53, 3356.
- [16] T.-J. Park, S. Sambasivan, D.A. Fischer, W.-S. Yoon, J.A. Misewich, S.S. Wong, *J. Phys. Chem. C* **2008**, 112, 10359.

- [17] E. Ressouche, V. Simonet, B. Canals, M. Gospodinov, V. Skumryev, *Phys. Rev Lett.* **2009**, 103, 267204.
- [18] A.K. Singh, S.D. Kaushik, B. Kumar, P.K. Mishra, A. Venimadhav, V. Siruguri, S. Patnaik, *Appl. Phys. Let.* **2008**, 92, 132910.
- [19] D. Voll, A. Beran, H. Schneider, *Phys. Chem Minerals* **2006**, 33, 623.
- [20] R. Arpe, H.K. Müller-Buschbaum, *J. Inorg. Nucl. Chem.* **1977**, 39, 233.
- [21] E. Kostiner, G.L. Shoemaker, *J. Solid State Chem.* **1971**, 3, 186.
- [22] J. Rodriguez-Carvajal, *Fullprof Program, version 2.4.2*; ILL Grenoble, Grenoble, France, **1993**.
- [23] K. Lagarec, D.G. Rancourt, *Recoil-Mössbauer Spectral Analysis Software for Windows, Version 1.02*; Department of Physics, University of Ottawa, Ottawa, Canada, **1998**.
- [24] F. Menil, *J. Phys. Chem. Solids* **1985**, 46, 763.
- [25] V.A. Bokov, G.V. Novikov, V.A. Trukhtanov, S.I. Yushchuk, *Soviet Physics-Solid State* **1970**, 11, 2324.
- [26] V.A. Bokov, S.I. Yushchuk, G.V. Popov, N.N. Perfenova, A.G. Tutov, *Soviet Physics-Solid State* **1971**, 13, 1333.
- [27] J. De Sitter, C. Dauwe, E. De Grave, A. Govaert, G. Robbrecht, *Physica* **1977**, 86-88B, 919.
- [28] D. Groult, M. Hervieu, N. Nguyen, B. Raveau, *J. Solid State Chem.* **1988**, 76, 248.
- [29] Y. Zhang, *Inorg. Chem.* **1982**, 21, 3886.
- [30] F. Van der Woude, G.A. Sawatzky, A.H. Morrish, *Phys. Rev.* **1968**, 167, 533.
- [31] R.D. Shannon, *Acta Crystallographica A* **1976**, 32, 751.

Tables

Table 1: Crystal structure parameters of $\text{Bi}_2\text{Fe}_2\text{Al}_2\text{O}_9$.

Parameters				
Empirical Formula		$\text{Bi}_2\text{Fe}_2\text{Al}_2\text{O}_9$		
Crystal system		Orthorhombic		
Space group		<i>Pbam</i> (No. 55)		
Volume, $\text{\AA}^3$		382.01(4)		
a, $\text{\AA}$		7.8658(5)		
b, $\text{\AA}$		8.2877(5)		
c, $\text{\AA}$		5.8599(4)		
Atomic Positions		x	y	z
Bi – 4g		0.1736(2)	0.1685(2)	0.0000(0)
Fe_1 – 4f		0.5000(0)	0.0000(0)	0.2646(1)
Fe_2 – 4h		0.3582(7)	0.3434(1)	0.5000(0)
Al_1 – 4f		0.5000(0)	0.0000(0)	0.2646(1)
Al_2 – 4h		0.3582(7)	0.3434(1)	0.5000(0)
O_1 – 2b		0.0000(0)	0.0000(0)	0.5000(0)
O_2 – 8i		0.3771(1)	0.2174(1)	0.2489(2)
O_3 – 4g		0.1475(2)	0.4024(3)	0.5000(0)
O_4 – 4h		0.1591(2)	0.4324(2)	0.0000(0)
R_p , %		8.83		
R_{wp} , %		11.7		
R_{exp} , %		6.32		
χ^2		3.44		

Table 2: Mössbauer parameters of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions at room temperature. Isomer shift (IS/mm s^{-1}) relative to α -Fe, quadrupole splitting (QS/mm s^{-1}), linewidth (Γ /mm s^{-1}).

x	Sites	IS (mm/s)	QS (mm/s)	Γ (mm/s)
1	Tetra	0.230(2)	0.938(4)	0.134(3)
	Octa	0.344(2)	0.368(4)	0.130(3)
0.9	Tetra	0.225(2)	0.947(3)	0.141(2)
	Octa	0.342(2)	0.398(3)	0.142(3)
0.8	Tetra	0.222(3)	0.962(6)	0.155(5)
	Octa	0.339(3)	0.429(6)	0.155(6)
0.7	Tetra	0.220(2)	0.964(4)	0.146(3)
	Octa	0.333(2)	0.457(4)	0.148(4)
0.5	Tetra	0.213(3)	0.993(6)	0.162(4)
	Octa	0.328(3)	0.495(6)	0.163(5)
0.3	Tetra	0.198(3)	1.014(6)	0.153(5)
	Octa	0.320(3)	0.534(6)	0.172(5)
0.2	Tetra	0.194(3)	1.020(6)	0.151(5)
	Octa	0.318(3)	0.541(5)	0.160(4)
0.1	Tetra	0.195(9)	1.03(2)	0.196(2)
	Octa	0.321(7)	0.544(1)	0.174(1)

Table 3: Cation distributions in $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions.

Sites	x	Site population of iron from Rietveld refinement (%)	Mössbauer subspectral area (%)
Tetra	0.1	46.0	45.9(4)
	0.2	44.5	45.3(2)
	0.3	43.5	45.1(2)
	0.5	49.2	50.0(2)
	0.7	51.2	51.6(1)
	0.8	50.7	52.4(2)
	0.9	50.0	51.6(9)
	1.0	50.1	51.1(9)
Octa	0.1	54.0	54.1(4)
	0.2	55.5	54.7(2)
	0.3	56.5	54.9(2)
	0.5	50.8	50.0(2)
	0.7	48.8	48.4(1)
	0.8	49.3	47.6(2)
	0.9	50.0	48.4(8)
	1.0	49.9	48.9(9)

Figure captions

Figure 1: Crystal structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (space group *Pbam*) consisting of chains of edge-connected FeO_6 octahedra parallel to the c-axis which are interconnected by Fe_2O_7 double tetrahedra.

Figure 2: A representative EDX spectrum of $\text{Bi}_2\text{Fe}_2\text{Al}_2\text{O}_9$.

Figure 3: Room temperature XRD patterns of selected $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions prepared by the mechanochemical/thermal synthesis.

Figure 4: Rietveld refinement of the $\text{Bi}_2\text{Fe}_2\text{Al}_2\text{O}_9$ solid solution ($x = 0.5$).

Figure 5: Lattice parameters of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions at room temperature. The solid line represents the behaviour expected according to Vegard's law.

Figure 6: Mössbauer spectra of selected $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions taken at room temperature for (a) $x = 0.1$, (b) $x = 0.3$, (c) $x = 0.5$, (d) $x = 0.7$, and (e) $x = 1.0$. Subspectral area fractions (%) are also given.

Figure 7: Isomer shifts in $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions versus iron content for (top) tetrahedral and (bottom) octahedral sites. Lines drawn to guide the eye.

Figure 8: Quadrupole splittings in $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions versus iron content for (top) tetrahedrally and (bottom) octahedrally coordinated sites. Lines drawn to guide the eye.

Figure 9: Ratio of iron populations, $N(\text{Fe}_\text{O})/N(\text{Fe}_\text{T})$, in octahedrally and tetrahedrally coordinated sites of $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solutions determined from (triangles) XRD and (squares) Mössbauer data, room temperature.

Figure 10: Re-equilibration of a non-equilibrium cation distribution for a $\text{Bi}_2(\text{Fe}_x\text{Al}_{1-x})_4\text{O}_9$ solid solution with $x = 0.5$: (a) non-equilibrium cation distribution with $N(\text{Fe}_\text{O})/N(\text{Fe}_\text{T}) \approx 0.45$ created by high-energy milling. (b) distribution with $N(\text{Fe}_\text{O})/N(\text{Fe}_\text{T}) \approx 1.05$ after 0.5 h annealing at 800°C . Spectra taken at room temperature.

Graphics

Figure 1: Crystal structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ (space group $Pbam$) consisting of chains of edge-connected FeO_6 octahedra parallel to the c -axis which are interconnected by Fe_2O_7 double tetrahedra.

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