Bi-apatite: Synthesis, crystal structure and low-temperature heat capacity

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ABSTRACT

In the present study, we describe a new approach to the synthesis of a Bi-containing apatite, which allows for a reduced reaction time and temperature. Using *in-situ* variable temperature X-ray diffraction measurements, we have refined the crystal structure of the material, which shows that its composition may be described as $[Ca_{3.88\pm0.01}Bi_{0.12\pm0.01}]^F[Ca_{4.42\pm0.01}Bi_{1.58\pm0.01}]^T(PO_4)_6O_{1.85\pm0.01}$. The compound displays isotropic thermal expansion in the temperature range (173–373) K. A thermodynamic investigation of the sample was undertaken, which revealed the low-temperature heat capacity, $C_{p,m}^o$, which was determined using adiabatic calorimetry from $T = 6.4$ K to 305.0 K. Smoothed $C_{p,m}^o(T)$ values between 6.5 K and 305.0 K are presented, along with the functions $[S_m^o(T) - S_m^o(6.5)]$, $[H_m^o(T) - H_m^o(6.5)]$, and $[\Phi_m^o(T) - \Phi_m^o(6.5)]$. Possible causes of the abnormal increase on the heat capacity curve in the low-temperature region are discussed.

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1. Introduction

Apatites have general formula $A_2^F A_3^T (BO_4)_3 X$, where A are mono- (Na, K, *etc.*), di- (Ca, Sr, Ba, *etc.*), tri- (Ln, Y), or tetravalent (Th, U) cations in various combinations; B are tetravalent (Si, Ge), pentavalent (P, As, V, Cr, Mn), or hexavalent (S) ions; and X are usually halogens, hydroxyl, or oxygen [1,2]. Due to one of the highest isomorphic capacity among all mineral types apatite materials can be applied in different areas of industry [3].

One of the most topical field of using apatite materials is in biomaterials applications because substituted hydroxyapatite (idealized formula $Ca_5(PO_4)_3OH$) is the main mineral component of natural bones and teeth of mammals [4]. Nowadays, hydroxyapatite-based materials are existing in different forms: from powders to ceramics [5,6]. To improve biological activity of apatite-based materials chemical substitutions can be utilised. Such examples can be derived by the incorporation of bismuth and antimony in apatite structure, which are well known as antimicrobial agents [7,8]. There are however few reported examples in this field, and most investigations were concentrated on the antimicrobial properties and cytotoxicity of such materials [9,10]. However, in order to solve real practical and technological problems, there must be data on the physico-chemical characteristics of the materials in addition to deriving information on the proper-
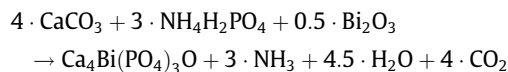
ties of matter useful from the point of view of materials science. The lack of such information makes it difficult to create new functional materials due to the difficulty of predicting the physical behaviour of this substance in the process of practical application.

In present study, we introduce the results of structural and thermodynamics properties of a Bi-containing apatite, which can be used for correction of content of bioactive elements in apatite structure and calculation of thermodynamics of biological process in aim to control them.

2. Experimental

2.1. Synthesis

Previous reports of the synthesis of $Ca_4Bi(PO_4)_3O$ were carried out using stochiometric mixture of calcium carbonate, bismuth oxide and ammonium dihydrophasphate in accordance with the following equation [11]:

$$4 \cdot CaCO_3 + 3 \cdot NH_4H_2PO_4 + 0.5 \cdot Bi_2O_3$$
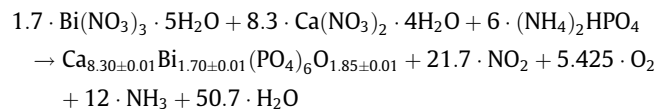$$\rightarrow Ca_4Bi(PO_4)_3O + 3 \cdot NH_3 + 4.5 \cdot H_2O + 4 \cdot CO_2$$

The duration of the synthesis was at 48 h at a sintering temperature of 1373 K.

In the present study, we used calcium nitrate tetrahydrate instead calcium carbonate with the aim of reducing the reaction time and temperature. This was possible because the decomposi-

tion temperature of calcium nitrate (834 K) is lower than that of calcium carbonate (1098 K). As a result, the calcium oxide with increased surface energy due to the high dispersity and defectiveness of the surface layer of particles forms and initializes the reaction at lower temperatures in according to the following equation:

$$1.7 \cdot Bi(NO_3)_3 \cdot 5H_2O + 8.3 \cdot Ca(NO_3)_2 \cdot 4H_2O + 6 \cdot (NH_4)_2HPO_4$$

$$\rightarrow Ca_{8.30\pm0.01}Bi_{1.70\pm0.01}(PO_4)_6O_{1.85\pm0.01} + 21.7 \cdot NO_2 + 5.425 \cdot O_2$$

$$+ 12 \cdot NH_3 + 50.7 \cdot H_2O$$

(Standard uncertainty for the composition is u = 0.01 for refined crystallographic positions).

The reaction mixture was calcined in a porcelain crucible at 573 K, after which the temperature was increased to 1223 K with 100 degree steps.

2.2. Sample characterization

Phase purity was confirmed by powder X-ray diffraction (PXRD) using a Shimadzu XRD-6000 diffractometer (Bragg-Brentano geometry) equipped with a CuKα X ray tube operated at 40 kV and 40 mA. The patterns were accumulated using a step size of 0.02° and a dwell time-per-step of 11 s. Samples were mounted in a top loaded trough, which was rotated during data collection. Under these conditions, the intensity of the strongest reflection was approximately 40 000 counts.

The experimental XRD-pattern was compared with patterns for compounds forming in Bi-Ca-P-O system ($Ca_3Bi(PO_4)_3$ [12], $Ca_{0.5}$-$Bi_3P_2O_{10}$ [13]) and other Bi-apatite compounds ($Sr_4Bi(PO_4)_3O$ [14] and $Ca_4Bi(VO_4)_3O$ [15]), which demonstrated that apatite-structured compound was obtained.

The elemental composition of the compound was determined by energy dispersive X-ray fluorescence analysis in air using a Wavelength Dispersive X-ray Fluorescence Spectrometer LAB CENTER XRF-1800 (Table 1). The elements that can be determined with this spectrometer range from Na to U. It is equipped with a thermoelectrically cooled semiconductor detector.

Rietveld refinement of the powder X-ray diffraction (PXRD) data was carried out from 10° to 140° 2θ using TOPAS V3 [16], using an initial structural model based on the hydroxyapatite crystal structure reported by Saenger et al. [17]. A pseudo-Voight peak shape function modelled the Bragg reflections and a four-coefficient Chebychev polynominal and 1/x profile background, a zero error, scale factors and lattice dimensions were refined sequentially. The Ca/Bi occupancies were refined, followed by the atomic positions and isotropic atomic displacement parameters (ADPs) in groups as follows: framework A^I cations, tunnel A^{II} cations; P; and all oxygen ions (framework and tunnel). Structural investigations of the sample were carried out on the same diffractometer equipped with an Anton Paar TTK450 cooling attachment.

The low-temperature heat capacity, $C_{p,m}^o$, was determined using adiabatic calorimetry over the temperature range from T = 6 K to 305 K for synthesized Bi-apatite. The measurements were conducted using a "AK-9.02/BCT-21"-type calorimeter (TERMAX, Russia). The experimental uncertainty was determined from previous heat-capacity measurements made on benzoic acid (mass fraction purity 0.99998) and synthetic sapphire, α-Al_2O_3 (mass fraction

purity 0.99999). The $C_{p,m}^o$ results between T = 5 K and 330 K on the benzoic acid which were compared to published values [18] are shown in Supplementary Fig. S1. The $C_{p,m}^o$ results between T = 5 K and 273 K on the synthetic sapphire, which were compared to published values [19] are shown in Supplementary Fig. S2. The agreement is better than 0.4% at T > 20 K and 2.0% at T < 20 K for benzoic acid and better than 0.2% at T > 30 K and 2.0% at T < 30 K for sapphire. We conclude that, with this calorimeter and our experimental set-up, that $C_{p,m}^o(T)$ can be determined with the combined expanded uncertainty, U_c, is $U_{c,r}(C_p°)$ = 0.02 for T < 15 K, 0.005 from T = 15 K to 40 K, 0.002 between T = 40 K and 330 K at the 0.95 level of confidence (k = 2).

The heat capacity of the apatite samples was measured on pelletized powders with masses of 0.977 g in the 1st series and 1.101 g in the 2nd series. Liquid nitrogen and helium were used to reach cryogenic temperatures in two different sets of $C_{p,m}^o(T)$ determinations. One set of data was collected between T = 78 K to 305 K and the other from T = 6 K to 85 K. For the measurements, an evacuated titanium ampoule containing the sample pellet was closed and hermetically sealed using indium and then filled with dry helium to serve as a heat exchanger (room temperature and 0.008 MPa pressure). Further details on the construction of the calorimeter and the experimental procedures are given in reference [20].

3. Results and discussion

3.1. Crystal structure

Using the synthesis conditions described, PXRD revealed a single-phase sample with reflections consistent with those expected for a hexagonal apatite structure in the space group $P6_3/m$. A Rietveld refinement proceeded smoothly to yield a good match to the experimental data and the refined atomic positions and selected bond lengths are listed in Tables 2 and 3 respectively. An image of the experimental Rietveld fitting for the XRD data collected at room temperature is shown in Fig. 1 with the variation in lattice parameters determined at each temperature shown in Table 4.

The Rietveld refinement indicated the Bi ions are located at the A^{II} (6h) tunnel position, which is a similar finding to other Bi containing apatites [21] ($Bi_2La_8(GeO_4)_6O_3$) and Bi-containing apatite polysomes (i.e. $Pb_{15-x}Bi_{x/2}Na_{x/2}(Ge_2O_7)_3(GeO_4)_3$ x = 0, 3 & 6) [22]. In addition, this work provides further evidence that more highly charged ions accumulate at the channel site, as recently confirmed for a Th^{4+} containing apatite [23].

The refined cation stoichiometry of $Ca_{8.30\pm0.01}Bi_{1.70\pm0.01}$ gives a slightly lower bismuth content compared to that expected from the experimental procedure, which could indicate a small amount of Bi volatilization. However, the refinement procedure assumed a full occupancy of both A sites and the presence of cation vacancies on the A^F sites has been observed previously in apatite structure-types [24]. This could be another possible reason for this deviation. Alternatively, the refined cation stoichiometry gives a chemical formula of $Ca_{8.30\pm0.01}Bi_{1.70\pm0.01}(PO_4)_6O_{1.85\pm0.01}$, which additionally required the presence oxygen vacancies in the channel oxygen positions to enable charge balancing. Nevertheless, the calculated

Table 1
X-ray fluorescence analysis data for $Ca_{8.30}Bi_{1.70}(PO_4)_6O_{1.85}$ (Z = 1)[a].

Compound	CaO/wt%		Bi₂O₃/wt%		P₂O₅(wt%)	
	Found	Calculated	Found	Calculated	Found	Calculated
$Ca_{8.30}Bi_{1.70}(PO_4)_6O_{1.85}$	36.27	36.16	30.75	30.77	32.98	33.08

[a] Standard uncertainties u are u(wt) = 0.02%.