



Vibrational spectra of a baghdadite synthetic analogue



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ABSTRACT

Single $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ phase, baghdadite, was synthesized by the standard ceramic route at a high temperature. Calcium zirconosilicate, $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, was characterized by FT-IR and Raman spectroscopy. The *ab initio* calculations of IR and Raman spectra for the baghdadite crystal structure were carried out by means of the Crystal09 program. The obtained results were used in the analysis of experimental vibrational spectra of baghdadite samples.

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1. Introduction

Baghdadite, $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, a new calcium zirconium silicate mineral has been discovered in melilite skarn in contact with banded diorite from the Qala-Dizeh region, NE Iraq, and characterized by Al-Hermezi et al. [1]. Baghdadite is a rare mineral belonging to the cuspidine group. It has been found in Japan from garnetvesuvianite skarns [2] and gahlenite-spurite skarns [3], in Norway from melilite skarns [4] in Russia from skarned carbonate xenoliths [5] and probably in Canary Islands [6]. An incongruently melting ternary compound calcium zirconosilicate, $\text{Ca}_3\text{ZrSi}_2\text{O}_9$, is the ternary phase in the $\text{CaO-ZrO}_2\text{-SiO}_2$ system, besides calcium zirconium silicate, $\text{Ca}_2\text{ZrSi}_4\text{O}_{12}$ [7,8]. It was found to melt at 1600°C with the formation of new solid phases (Ca_2SiO_4 and ZrO_2) and a liquid with composition different from the original phase. As it has been reported in the literature, the synthetic analogue $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ of baghdadite has demonstrated a good bio-compatibility profile [9] and shows a bright yellow fluorescence under UV excitation [10]. $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ is an important constituent of $\text{CaO-ZrO}_2\text{-SiO}_2$ refractories. New research reveals that $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ plays a key role as transitory phase during reaction sintering of lime-zircon and dolomite-zircon mixtures [11]. The crystal structures of the synthetic compound $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ and $\text{Ca}_3\text{HfSi}_2\text{O}_9$ were solved and refined by Plaisier et al. [12] using neutron and X-ray powder diffraction data. The result of the structural determination of

baghdadite was the unusual cationic distribution in the octahedral walls of baghdadite, with the consequence violation of the fourth Pauling rule [12,13].

To date, there is no comprehensive approach to vibrational spectroscopy studies of baghdadite, and it is the aim of our work to synthesize, monophase baghdadite polycrystal as checked by XRD analysis and carry out the measurements of its IR and Raman spectra together with detailed analysis and bands assignment based on the results of theoretical *ab initio* calculations conducted by means of the Crystal09 program.

2. Experimental

$\text{Ca}_3\text{ZrSi}_2\text{O}_9$ was prepared using a powder mixture of calcium carbonate (98.81%, CaCO_3 , Chempur, Poland), zirconium dioxide (98.50%, ZrO_2 , Across Organics, Belgium), and silicon dioxide (96.5%, SiO_2 , Chempur, Poland) with a molar ratio of 3:1:2, $\text{CaO/ZrO}_2/\text{SiO}_2$ as raw materials, respectively. The mixture was calcined at 1200°C for 5 h. The starting material was crushed, mixed in water-free isopropanol and milled in agate mortar for 30 min. This method was used to avoid segregation of oxides during drying. After drying and sieving to powders with a particle diameter up to $63\ \mu\text{m}$, these were mixed with 6% (w/v) polyvinyl alcohol (PVA, Sigma-Aldrich, USA). The batch was uniaxially pressed at 40 MPa to produce green cylinders with a diameter of 20 mm and comparable in height. Subsequently, the green cylinders were heated in an electric furnace to 1500°C with a constant heating rate of $10^\circ\text{C}\ \text{min}^{-1}$ and sintered at 1500°C for 5 h and then cooled with the furnace.

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The phase composition was determined by XRD utilizing an equipment by PANalytical X'Pert Pro MPD operated at 40 KV and 40 mA using Cu K α radiation. The specimens were scanned over an angular range $10^\circ < 2\theta < 140^\circ$ with steps $0.008^\circ/s$. FT-IR spectra were recorded with a Bruker Company Vertex 70v spectrometer. Spectra were collected in the mid (MIR) ($4000\text{--}400\text{ cm}^{-1}$) and far infrared (FIR) ($400\text{--}100\text{ cm}^{-1}$) regions using 128 interferogram scans at 4 cm^{-1} resolution. Samples were prepared by the standard KBr (MIR) and polyethylene (FIR) pellet methods. Raman studies were carried out using a Horriba Yvon Jobin LabRAM HR micro-Raman spectrometer equipped with a CCD detector. An excitation wavelength of 532 nm was used and the beam intensity was about 10 mW. The acquisition time was set to 30 s.

3. Results and discussion

3.1. Characterization of the baghdadite

Fig. S1, the Supplementary material, shows the XRD pattern of the sample, the appearance of the peaks confirmed the formation of $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ and all the observed peaks could be indexed to the $P 2_1/c$ (14) space group (number) with monoclinic symmetry. The XRD pattern was refined by the Rietveld method and by using the HighScorePlus program. The XRD peaks were generated by using the $P 2_1/c$ (14) space group (number) with monoclinic symmetry (Fig. S2 in the Supplementary material [14]). The pseudo-Voigt

function was chosen for the profile shape refinement. The refinement was carried out by allowing the variation of different parameters such as, cell parameters, scale factors, position parameters and isotropic thermal parameters.

The position of the Ca, Zr, Si and O atoms are given in the Supplementary material Table S1. The refined cell parameters are found to be $a = 7.36025(6)\text{ \AA}$, $b = 10.17641(4)\text{ \AA}$, $c = 10.45135(1)\text{ \AA}$. The unit cell volume is found to be 782.7239 \AA^3 . The goodness of fit parameters are found to be 1.9396 [15]. The results of the structural determination and refinement of synthesized $\text{Ca}_3\text{ZrSi}_2\text{O}_9$ from intensity data are in good agreement with those of the structural study of Plaisier et al. [12] (Table 1).

3.2. Ab initio calculations of IR and Raman spectra

The *ab initio* calculations of IR and Raman spectra have been carried out by means of the Crystal09 program [16–18]. The initial crystal structure parameters measured for synthesized baghdadite were applied for the geometry optimization, and the optimized crystal structure (the Supplementary material Table S2) was used later for vibrational spectra calculations.

The calculations have been done within the DFT formalism, with PBE exchange correlation potentials [19], level shift of 0.3 a.u., density mixing factor equal to 30%, reciprocal lattice grid of $8 \times 8 \times 8$ (170 *k* points in irreducible Brillouin zone) and basis sets: Ca [20], Zr [21], Si [22,23] and O [24], optimized for this particular

Table 1
X-ray powder diffraction pattern of baghdadite.

Measurement						Literature [12]					
Position [$^\circ 2\theta$.]	<i>d</i> (Å)	Relative int.	<i>h</i>	<i>k</i>	<i>l</i>	Position [$^\circ 2\theta$.]	<i>d</i> (Å)	Relative int.	<i>h</i>	<i>k</i>	<i>l</i>
11.9691	7.38823	12.1	1	0	0	12.0170	7.35914	9.3	1	0	0
12.0920	7.31338	27.4	0	1	–1	12.1300	7.29076	29.4	0	1	–1
14.7957	5.98251	8.0	1	1	0	14.8430	5.96338	8.4	1	1	0
16.9651	5.22209	15.5	1	1	–1	17.0140	5.20716	18.1	1	1	–1
20.6399	4.29987	14.9	1	0	–2	20.6810	4.29136	17.2	1	0	–2
21.1620	4.19494	15.1	1	2	0	21.2110	4.18540	15.6	1	2	0
22.8991	3.88050	14.2	1	2	1	22.9400	3.87375	14.7	1	2	1
25.6712	3.46740	8.1	2	1	0	25.7250	3.46034	8.8	2	1	0
						27.1610	3.28051	5.3	1	2	–2
27.5781	3.23182	27.9	0	3	1	27.6240	3.22657	27.3	0	3	1
28.9086	3.08604	8.0	1	3	0	28.9590	3.08077	8.7	1	3	0
29.3965	3.03592	100.0	2	0	–2	29.4520	3.03028	100.0	2	0	–2
29.8298	2.99280	9.0	1	1	3	29.8410	2.99167	9.1	1	1	3
29.8623	2.98962	86.9	2	0	2	29.8890	2.98702	92.8	2	0	2
30.7052	2.90944	11.2	2	1	–2	30.7610	2.90427	10.5	2	1	–2
						31.0640	2.87666	5.4	2	2	–1
31.0669	2.87639	32.5	0	2	3	31.0900	2.87432	31.7	0	2	3
31.1532	2.86861	11.9	2	1	2	31.1810	2.86612	14.4	2	1	2
						31.2730	2.85794	6.8	2	2	1
31.3776	2.84861	44.4	0	3	2	31.4160	2.84524	46.8	0	3	2
35.1957	2.54784	8.0	0	4	0	35.2470	2.54425	7.7	0	4	0
35.9246	2.49780	24.9	2	3	0	35.9800	2.49411	27.4	2	3	0
36.2519	2.47599	7.6	2	1	–3	36.3020	2.47271	8.6	2	1	–3
36.8322	2.43831	11.2	2	1	3	36.8460	2.43745	10.9	2	1	3
36.8779	2.43539	9.0	2	3	–1	36.9370	2.43166	8.4	2	3	–1
37.0694	2.42325	7.9	2	3	1	37.1160	2.42032	7.7	2	3	1
39.4571	2.28193	7.8	2	2	–3	39.5080	2.27912	8.1	2	2	–3
39.9977	2.25233	7.4	2	2	3	40.0150	2.25142	7.3	2	2	3
						44.2050	2.04723	5.3	0	1	–5
44.3661	2.04017	18.9	2	3	–3	44.4190	2.03788	19.1	2	3	–3
44.8582	2.01892	18.3	2	3	3	44.8800	2.01801	18.6	2	3	3
						45.3570	1.99785	6.1	0	5	–1
49.4377	1.84209	38.0	4	0	0	49.5040	1.83979	39.3	4	0	0
50.2292	1.81490	22.7	2	3	–4	50.2740	1.81339	23.6	2	3	–4
50.8262	1.79498	20.6	2	3	4	50.8340	1.79473	21.2	2	3	4
51.1932	1.78297	9.0	2	5	0	51.2520	1.78107	8.0	2	5	0
53.1298	1.72245	23.1	2	2	–5	53.1630	1.72145	23.4	2	2	–5
53.8465	1.70120	26.4	2	2	5	53.8350	1.70154	25.1	2	2	5
						54.7850	1.67425	5.3	0	6	–1
						57.5000	1.60148	5.1	4	3	–1

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