Structural Studies of Layered Zirconosilicate $Na_2Zr_7Si_{2.5}O_{20}\cdot3H_2O$ and Its Ion Exchanged Forms

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A new zirconosilicate of chemical formula $Na_2Zr_7Si_{2.5}O_{20}\cdot3H_2O$ and its K and Ba ion–exchanged forms are characterized by means of X-ray diffraction, TG-DTA and HRTEM analyses. Preliminary information about space group and unit cell parameters is reported. The structural peculiarities of the studied compound are compared with those of other previously reported zirconium compounds, with similar powder diffraction patterns and unknown crystal structures. An arrangement of the zirconium polyhedra within the crystal structure of these materials is proposed.

Key words: zirconosilicate, layered structure, electron diffraction

1. INTRODUCTION

Physical and chemical properties of microporous titanosilicates and zirconosilicates attracted great attention during the last decades. The intensive studies resulted in obtaining of a large number of new compounds with various chemical compositions and crystal structures. Among them, layered materials are poorly studied, although some recent investigations have demonstrated their potential application in catalysis, adsorption and ion-exchange [1,2]. Hydrothermal synthesis and some characteristics of the title compound were reported by Kostov-Kytin and Kalvachev in 2004 [3]. Compounds with similar powder diffraction patterns and slightly different chemical composition $Na_xZr_ySi_zO_w$ (x = 1 – 5, y = 4 – 6, z = 2 – 5 and w = 15 – 25) were synthesized and some of their physical properties were described by Suzan Lambert in her patent from 1994 [4]. The author has pointed out the potential catalytic properties of those materials, because of their good ion exchange capacity and high surface area (80 – 400 m^2/g) which favors dispersion of metals on it.

Later on in 1997 and 1998 Bortun et al. reported syntheses and amine-intercalation properties of zirconium compounds with similar powder diffraction patterns: $Na_2Zr_5Si_2O_{15}\cdot3H_2O$ [5], $Na_2Zr_5Ge_2O_{15}\cdot4H_2O$ [6], $Zr_2O_3(HPO_4)\cdot1.5H_2O$ [7], $Zr_2O_3(HAsO_4)\cdot1.5H_2O$ [8]. The diffraction patterns of all of the reported compounds do not differ substantially from each other except for the first peak position, which varies between 12.21 Å for $Na_2Zr_7Si_{2.5}O_{20}\cdot3H_2O$ and 15.1 Å for the zirconium germanate phase. In fact, the position of the first peak has been reported to be different for the initial, for the "hydrogen" form and the intercalated samples of the reported compounds, while the rest of the powder

diffraction peaks remain in almost the same positions. Such peculiarity was explained as being due to the layered character of the reported compounds [6].

Farther structural investigations have been hindered by the small grain size and low degree of crystallinity of these materials. Although the chemical compositions of the reported compounds slightly differ from that of the compounds studied here, the similarity of their XRD patterns is indicative for the isomorphism of their layers. Moreover, due to the high Zr : Si (Ge, P, As) ratio and the presence of differently charged tetrahedral units it could be expected that the layers are mainly composed by zirconium polyhedra. Such zirconium compounds are very interesting from the viewpoints of both material science and crystallography. In order to obtain more information concerning the crystal structure of the title compound, we performed XRD, TG–DTA and HRTEM analyses and here we present the preliminary results of that study.

2. EXPERIMENTAL

2.1. Syntheses: The studied compound was hydrothermally synthesized following a procedure described by Kostov-Kytin and Kalvachev [3]. In a typical run, 0.27 g of SiO_2 (highly dispersive, extra pure, MERCK) was added to a solution of 3.5 g NaOH (WAKO) and 40 mL distilled water. A 2.59 g of $ZrCl_4$ (99.95% WAKO) were solved in 20 mL distilled water. Both solutions were heated up to boiling temperature and mixed together. The obtained white gelatinous precipitation was allowed to homogenize for 1 hour. The gel was then transferred to 25 mL teflon-lined containers, placed in a stainless steel pressure vessel and heated in a 200°C oven for 168 hours. The product was

washed several times with distillated water and dried at 40°C for 12 h. The chemical composition was obtained on the basis of electron microprobe analyses. Potassium and Barium ion-exchanged samples were prepared by treatment of the initial Sodium compound with 0.1 M(mol/L) solution of the corresponding chloride for 3 days at 60°C. The solution has been changed 3 times per day.

2.2. Analytical procedures: The powder XRD data were collected in a step-scan regime (0.02° and time 2 s) on a MXP3 (MAC Science Co.Ltd) diffractometer with Cu Kα radiation in the range 2θ, 5–80°. Thermal analyses were performed on a TG–DTA2000S (MAC Science Co.Ltd) in static air and heating rate of 10°/min. The electron diffraction(ED) patterns and high resolution (HR) lattice images were obtained by a JEM2010F (JEOL) 200 kV TEM.

3. RESULTS AND DISCUSSION

The studied compound was obtained as a white powder composed of tiny flakes with an area of about 1 μm² and nanosized thickness as shown in Fig.1.
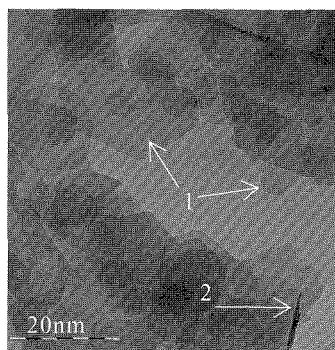

Fig.1. TEM image of the studied compound. The numbers pointed at crystallites with different orientation to the sample surface: 1 – parallel to the sample surface; 2 – almost vertical to the surface.

Powder diffraction patterns of the as synthesized compound and its K and Ba ion exchanged forms are presented in Fig.2. Although the electron microprobe analyses confirm successful ion exchange of the studied compound, the positions of the first peak do not differ
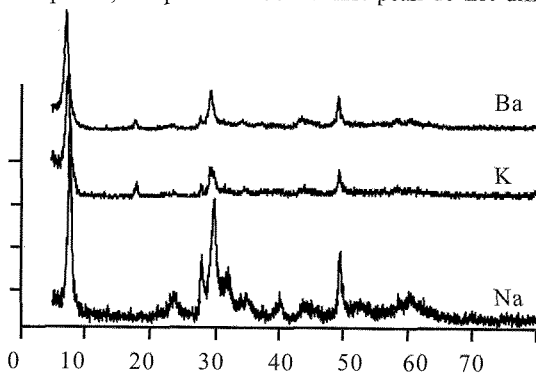

Fig.2. XRD pattern of initial – Na and its K and Ba ion exchanged samples.

substantially and have values of 11.56, 11.76 and 12.08 Å, respectively, for the as-synthesized sodium compound and its K and Ba ion-exchanged forms. In contrast, values of 11.7 and 12.3 Å were reported for the first peak of Na$_2$Zr$_5$Si$_2$O$_{15}$·3H$_2$O and its K–exchanged form [4]. Except for the first peak displacement towards the lower 2θ region, an additional peak at d = 4.92 Å appears within the XRD patterns of both ion-exchanged samples. The relative intensities of the rest of the peaks differ as well. However, the diffraction patterns are quite similar and give evidence of the previously proposed layered character of the crystal structure [4]. We could not compare our results with those of other authors, because of the scanty information they provided for the XRD patterns of the ion-exchanged forms except for the values cited above. It should be noted that the first peak position of the as-synthesised Na sample differs from previously reported as being 12.21 Å for the same compound [3]. However, as mentioned above, this peak is related to the interlayer space and its position is very sensitive to the hydration level of this compound. These differences are very likely due to variations in the post-synthetic treatment of the samples including the drying procedure. Similar relation between first peak position and synthetic conditions has been reported for Na$_2$Zr$_5$Si$_2$O$_{15}$·xH$_2$O (for x = 3 first peak is at 11.7 while for x = 4 first peak is at 15.0 Å [5].

The TG-DTA analyses of the initial and ion-exchanged samples show three step water liberation accompanied with five peaks in the DTG curves. For Na$_2$Zr$_7$Si$_{2.5}$O$_{20}$, DTG curve shows maxima at about 50, 80, 270, 340 and 390°C, but for the K and Ba exchanged samples the second and last ones are moved towards the higher temperature at about 130 and 420°C respectively Fig.3.

During the first stage (50 – 150°C) a quantity of about one water molecule is released for all of the
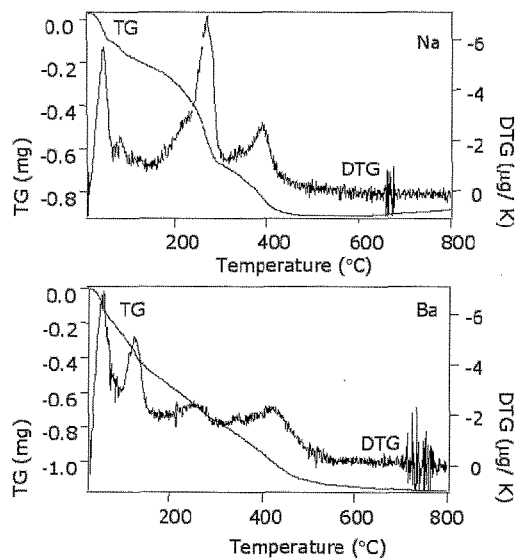

Fig.3. TG and DTA curves for initial – Na and Ba-exchanged samples.

studied compounds. This weight loss could be attributed to weakly bonded interlayer water. In the next stage (150 – 300°C), the amount of the released water is almost $2H_2O$ for the initial, and about $3H_2O$ for the ion-exchanged samples. These more strongly bonded interlayer water molecules are probably coordinated to the metal ions and their amount depends on the hydration capacity of the interlayer atoms. All of the studied compounds show the release of about one water molecule during the third stage (300 – 500°C).

The thermal behavior of the previously reported compounds with similar powder diffraction patterns is comparable. The amount of water release during the first step varies from 0.7 to 3.5 molecules per formula unit, while the position of first powder diffraction peak shifts to lower 2θ range values. The number of water molecules, coordinated to the Na ions is almost the same for all the reported compounds and it is released in a similar temperature range. During the third step the weight loss is almost the same for the Na compounds being always higher for the reported "hydrogen" forms.

The XRD patterns of the initial sample and samples thermally treated at 300, 500 and 800°C are given in Fig.4. As can be seen, the studied compound is
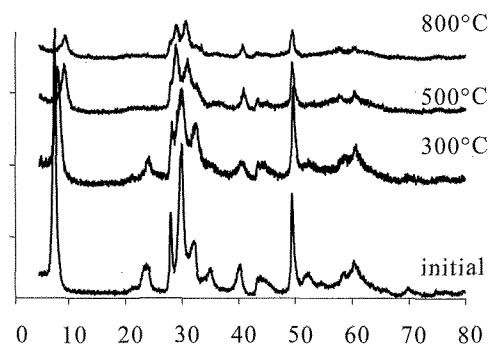

Fig. 4. XRD patterns of initial – Na and heated samples.

thermally stable up to about 300°C and only the first reflection shifts from 11.56 to 11.26 Å. This supports our assumption that the interlayer water release occurs in the temperature range 50-300°C. The samples recover all the water after 72 hours. Heating up to 500°C leads to changes in the relative intensities and more significant shift of some of the peaks (first peak shifts to 9.46 Å). This structure remains unchangeable up to 800°C. That process could be explained with the dehydration from OH groups which lead to irreversible changes of the crystal structure. Data, concerning the thermal stability of $Na_2Zr_5Si_2O_{15}\cdot3H_2O$ [5] and $Zr_2O_3(HPO_4)\cdot1.5H_2O$ [7] reveal the different behavior of these compounds. Although the zirconosilicate behaves similarly and remains stable up to 300°C, the authors reported complete change of its crystal structure upon higher temperature treatment and published diffraction data that differ substantially from ours. In contrast, the crystal structure of the zirconium phosphate compound remains practically the same even at 800°C, and only the first peak shifts from 10.4 to 10.3 Å. Despite the obvious

similarities of these compounds, one should be aware not only of their compositional but of their structural characteristics as well in order to better understand their thermal behavior.

The size and morphology of the studied compound contribute substantially to the broadening of powder diffraction peaks and intensity lowering for some of them. This makes it difficult to extract correct peak positions, which could be used in addition to calculate unit cell parameters of the studied compound. We managed to obtain cell parameters from a set of 15 reflexes using WinPLOTR software and indexing via DICVOL. The delivered monoclinic unit cell in P2/m and a = 11.58, b = 3.46 c = 23.11 Å, β = 91.3°.

ED patterns and HR lattice images were obtained for the initial (Na) and the Ba – exchanged compounds. The leaf-like morphology of the samples used for electron microscopy analyses caused preferred orientation of the crystallites parallel to the sample surface. Just occasional crystallites exhibit different, close to perpendicular orientation as illustrated in Fig.1. The electron microprobe analyses revealed identical chemical composition for both type oriented crystallites. It was possible to take ED patterns with good quality only for the crystallites of the first type (Fig. 5). The second type gave patterns where it is difficult to define individual diffraction spots (Fig.6). The analyses of distances confirmed only two of the lattice parameters and indicated a C-centered monoclinic cell and doubled b-parameter. Calculating the c-lattice parameter as a function of the first XRD peak position we came to two possible unite cells: a = 11.05, b = 6.4, c = 11.57 Å, ß = 92.0° (C2, Cm, C2/m) and a = 11.05, b = 6.4, c = 23.14 Å, ß= 92° (Cc, C2/c).

a=11.04, b=6.40 Å, γ=90.00°; h+k=2n

a=11.40, b=6.40 Å, γ= 88.96°; h+k=2n
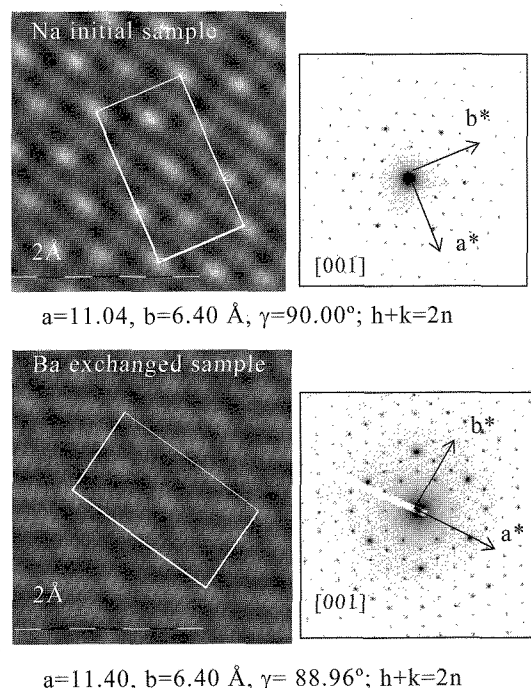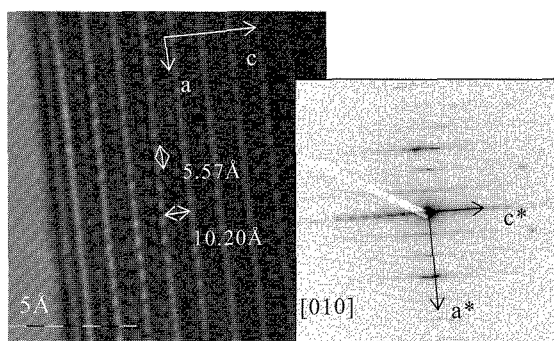
Fig. 5. HR images and ED patterns obtained from crystallites oriented parallel to the sample surface.

a=11.14, c=10.2 Å,   β~ 92°;   h=2n

Fig. 6. HR images and ED patterns obtained from a crystallite with close to the perpendicular orientation.

The Le Bail extraction and the whole profile structureless fit resulted in Rp 14.37% Rw 21.61% for C2/c, a = 11.18, b = 6.39, c = 23.08 Å, ß = 90.72°

The search within the structural data base for titanium and zirconium compounds with layered structures and unit cell parameters comparable with ours gave two interesting cases. The first one is that of the perrierite and chevkinite-type structures [9]. The compounds with such a structures have Ti:Si ratio >1. This structure type could explain the chemical composition of our compound. However, the octahedral coordination of Ti^{4+} together with the edge-sharing of its polyhedra in the proposed structures would hardly be acceptable in the case of Zr^{4+} since its bigger radius would not allow such connections without structure crucible distortions.

The second case is the mineral sabinaite $Na_4Zr_2TiO_4(CO_3)_4 \cdot xH_2O$ C2/c, a = 10.169, b = 6.616, c = 17.958 Å, ß = 94.14° (CCode 82488). The main building unit is a layer composed of edge-sharing ZrO_8

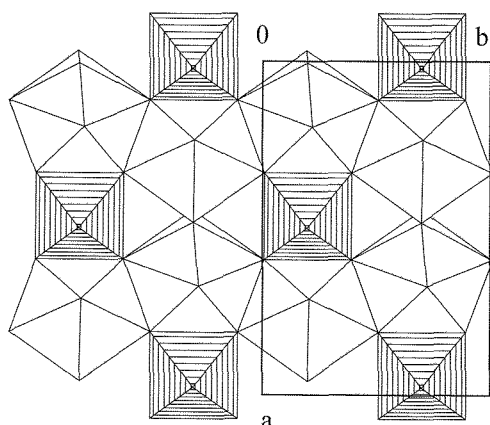and TiO_6 polyhedra as shown in Fig.7. This kind of layer construction seems more promising to understand the structure of the studied compound. Moreover the calculations based on the obtained lattice parameters and sabinaite atomic coordinates for Zr (Zr, Ti) and O gave very reasonable values for the inter-atomic distance (varying between 2.04 - 2.50 Å and 3.4 – 3.3 Å for Zr – O and Zr – Zr distances respectively).

Our preliminary conclusion is that the studied compound is built of sabinaite-like layers parallel to (110). The layers are composed of edge sharing ZrO_8 and ZrO_6 polyhedra. The SiO_4 groups decorate both sides of the layers and Na and H_2O molecules are situated within the interlayer space.

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Fig.7. Sabinaite type layer composed of edge-sharing TiO_6 and ZrO_8 polyhedra.