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Thermal behavior of $K_2MSi_3O_9 \cdot H_2O$ with the structure of umbite (M = Sn) and kostylevite (M = Pb) minerals

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Abstract

$K_2MSi_3O_9 \cdot H_2O$ (M = Sn, Pb) synthetic framework silicates are isotypical with umbite and kostylevite minerals, respectively. The silicate anion exhibits two structural types, one of which is an infinite chain polysilicate (umbite) and the other a cyclohexasilicate (kostylevite). The structural formulas may be written as $K_2Sn\{uB, 1_\infty{}^1\}[^3Si_3O_9]H_2O$ and $K_4Pb_2\{uB, 1r\}[Si_6O_{18}]2H_2O$. The thermal behavior of these compounds was determined by dynamic and isothermal thermogravimetry combined with powder X-ray diffraction between room temperature and 550 °C. The kostylevite-type compound presents a very rigid framework, the umbite-type structure being much more flexible. In both cases, the dehydration process takes place with a reduction in cell volume. Anhydrous tin silicate presents a monoclinic cell whose volume is almost invariant with temperature. $K_2PbSi_3O_9$ is obtained as an amorphous material. The structural characteristics of these phases are related to their ion exchange properties.
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1. Introduction

Silicates are the third largest class of chemical compounds after carbon compounds and oxides. The number of silicate minerals that occur in nature is very large [1]. At present, approximately one thousand natural silicates are known and about ten new ones are discovered on average each year. In addition, there are also several hundred synthetic silicates [2]. Silicate chemistry presents a wide range of structural units extending from discrete SiO_4 units to the tri-dimensional structures of tectosilicates, orthosilicates, and other more complex silicate species [3].

Recent years have seen an upsurge of interest in the study of inorganic materials with ion-exchange properties. Most of this work has centered on zeolites in conjunction with their use as detergent "builders" [4] and for the treatment of aqueous nuclear wastes [5,6]. These materials also are con-

venient model substrates for the extension of ion-exchange theory [7]. Their advantages lie in their highly selective cation-exchange properties, purity and reproducible stoichiometry. In addition their microporous nature promotes their well-known uses as catalysts and sorbents [8]. In all cases, understanding of the experimental behavior requires detailed knowledge of crystal structure.

Two decades ago, Ilyushin et al. described both orthorhombic [9] and monoclinic [10] natural polymorphs of $K_2ZrSi_3O_9 \cdot H_2O$. The orthorhombic form is known as umbite, while the monoclinic modification is the mineral kostylevite. More recently, umbite-type synthetic compounds have been reported: $K_2ZrSi_3O_9 \cdot H_2O$ as well as its ion-exchanged phases with sodium and cesium [11], $K_2TiSi_3O_9 \cdot H_2O$ [12,13], $K_2SnSi_3O_9 \cdot H_2O$ [14], and other materials with different levels of titanium–zirconium [15] or tin–zirconium [16] substitution. Some kostylevite-type materials have also been reported: $K_{1.26}H_{0.74}TiSi_3O_9 \cdot 1.8H_2O$ [17], $K_2PbSi_3O_9 \cdot H_2O$ [18], and a mixed potassium–sodium–titanium silicate [19].

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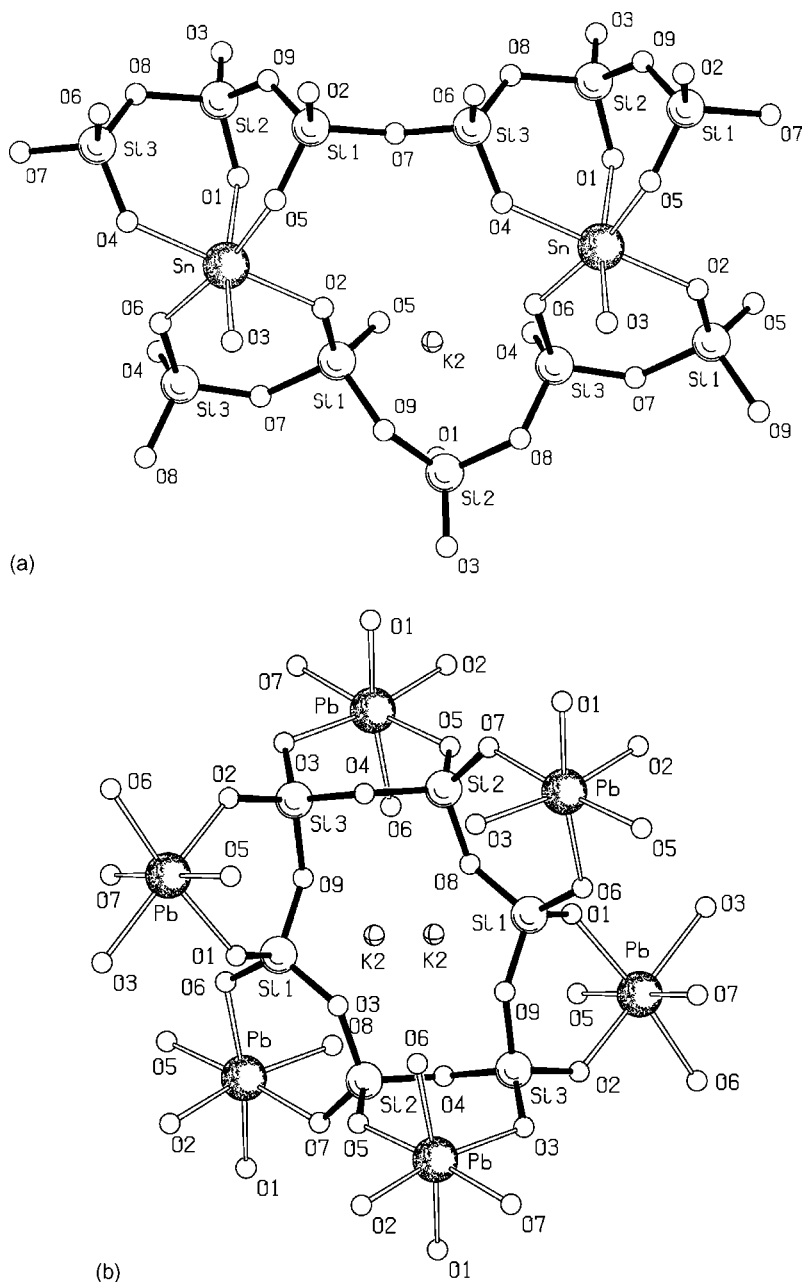*E-mail address:* jrgm@sauron.quoimica.uniovi.es (J.R. García).

Fig. 1. Crystal structures of both (a) umbite, which showed a channel formed by silicates and metal atoms, and (b) kostylevite, viewed lengthwise [1 1 0].

Both umbite and kostylevite are microporous framework solids possessing structures that consist of interlinked octahedra and tetrahedra and are raising considerable interest. Although the orthorhombic form is a long-chain polysilicate and the monoclinic form is a cyclohexasilicate, umbite and kostylevite exhibit a clear structural relationship (Fig. 1). However, their ion-exchange behavior is very different. All of the orthorhombic phases are excellent cation-exchangers [11,18,20], but the kostylevite variant is not [19]. In this paper, we put forward the proposition that this fact is related to the difference in flexibility of both umbite- and kostylevite-type structures.

2. Experimental

Hydrothermal crystallization of $K_2SnSi_3O_9 \cdot H_2O$ (umbite-type) was carried out employing the following method: 7.2 g of fused SiO_2 were dissolved in 34 mL of a 7 M KOH solution under stirring in a 100 mL Teflon-lined vessel. Subsequently, 3.5 mL of $SnCl_4$ were added drop-by-drop with stirring over the previous solution. The homogeneous solution was sealed and heated at 190 °C under autogenous pressure for 12 days. The solid was filtered off, washed with an excess of distilled water and dried in air at 70 °C. $K_2PbSi_3O_9 \cdot H_2O$ (kostylevite-type) was also obtained by

the hydrothermal method as previously described [19]. The tin, lead, silicon and potassium content of the solids was determined using SpectraSpec Spectrometer DCP-ACE. Anal. found (calculated data in brackets) for $K_2SnSi_3O_9 \cdot H_2O$:K 17.6 (17.64), Sn 26.9 (26.78), Si 18.9 (19.02); and for $K_2PbSi_3O_9 \cdot H_2O$:K 14.6 (14.71), Pb 38.6 (38.97), Si 15.9 (15.85). Dynamical thermogravimetric analysis was carried out at a rate of $10\,°C\,min^{-1}$ under a flow of nitrogen.

The room temperature X-ray patterns were collected using a Philips 1050 conventional powder diffractometer (Cu Kα, 40 kV and 30 mA) operating in Bragg-Brentano ($\theta/2\theta$) geometry. The samples were gently ground in an agate mortar and side-loaded into a holder in order to minimize the effects of preferred orientation. Data was collected over the angular range 9–110° 2θ with a step size of 0.02° (time constant 10 s). The patterns were indexed using the program TREOR [21] from twenty and seventeen low-angle accurately measured, unambiguous reflection positions. An orthorhombic cell was obtained for $K_2SnSi_3O_9 \cdot H_2O$:a = 10.085(5), b = 13.110(6), c = 7.159(4) Å (figures of merit M_{20} = 15 [22] and F_{20} = 26 (0.016, 51) [23]). A monoclinic cell was obtained for $K_2PbSi_3O_9 \cdot H_2O$: a = 6.554(2), b = 11.763(1), c = 13.028(5) Å, β = 103.57(2)° (figures of merit M_{20} = 17 [22] and F_{20} = 29 (0.0098, 71) [23]).

The high temperature X-ray patterns were collected using a Seifert XRD-3000 high resolution laboratory powder diffractometer (Cu Kα, 40 kV and 30 mA) operating in Bragg-Brentano (θ/θ) geometry, equipped with a Johanna Otto GmbH HDK S1 high temperature device. The samples were placed under vacuum (nominally 10^{-2} mPa) in a Pt–Rh rectangular can. Data was collected (angular range 9–60° 2θ, step size 0.02°, time constant 5 s) on heating in 50 °C intervals between 100 and 500 °C. A counting time of about 3 h was used for datasets, after an initial 10 min temperature equilibration period.

Ion exchange of cesium and strontium cations was studied using $0.05\,N\,MCl_n$–$M(OH)_n$ (M = Cs, Sr; n = 1, 2) solutions under batch conditions at V:m = 200:1 (mL:g), room temperature. The ratio of MCl_n to $M(OH)_n$ was varied from 9:1 to 1:9 and the pH measured at equilibrium with a WTW-538 pH meter. Concentrations of the cations in solution were measured using a Varian SpectrAA-300 atomic absorption spectrometer.

3. Results and discussion

$K_2SnSi_3O_9 \cdot H_2O$ is isostructural with umbite mineral. This structure (Fig. 1a) presents two different cationic positions, a water molecule, a tin atom, and a trisilicate group in the asymmetric unit. The trisylicate group $Si_3O_9^{6-}$ forms a long linear chain polysilicate, which would be represented as $[-O-SiO_2-]_n^{2n-}$. Thus, the structural formula may be written, according to Liebau's description [1], as $\{uB, 1_\infty^1\}[^3Si_3O_9]^{6-}$. On the other hand, $K_2PbSi_3O_9 \cdot H_2O$ has a kostylevite-type structure (Fig. 1b) with PbO_6 octahedra
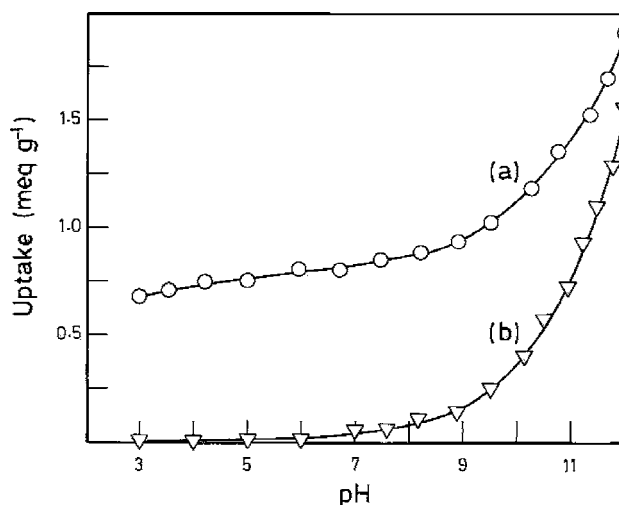
Fig. 2. Potentiometric titration of $K_2SnSi_3O_9 \cdot H_2O$ with (a) CsCl–CsOH and (b) $SrCl_2$–$Sr(OH)_2$.

and SiO_4 tetrahedra linked by vertex sharing to form a tri-dimensional framework. All non-water oxygen atoms belong to isolated $Si_6O_{18}^{12-}$ rings. Thus, the structural formula may be written as $Pb_2K_4\{uB, 1r\}[Si_6O_{18}] \cdot 2H_2O$ [1]. Both umbite- (orthorhombic) and kostylevite-type (monoclinic) structures exhibit the same octagonal, heptagonal and hexagonal distorted tunnels and windows delimited by edges from tetrahedra and octahedral alternating in exactly the same way. In addition, a clear correlation exists between orthorhombic (o) and monoclinic (m) cells (a_m-axis corresponding to c_o-axis, b_m to a_o and c_m to b_o). Nevertheless, their ion exchange properties are totally different. A number of static equilibrations of $K_2PbSi_3O_9 \cdot H_2O$ with Cs^+ and Sr^{2+} were carried out to assess the ability of these compounds to exchange K^+ for other cations. Almost no exchange was observed. This is in contrast with the behavior of $K_2SnSi_3O_9 \cdot H_2O$. Using this material, about $0.6\,meq\,g^{-1}$ of Cs^+ is taken up at a pH of 3 and the equilibrium uptake increases as a function of pH, reaching a maximum of $1.8\,meq\,g^{-1}$ at pH 12 (Fig. 2a). The exchanger shows lesser affinity for the strontium ion (Fig. 2b). Its uptake is
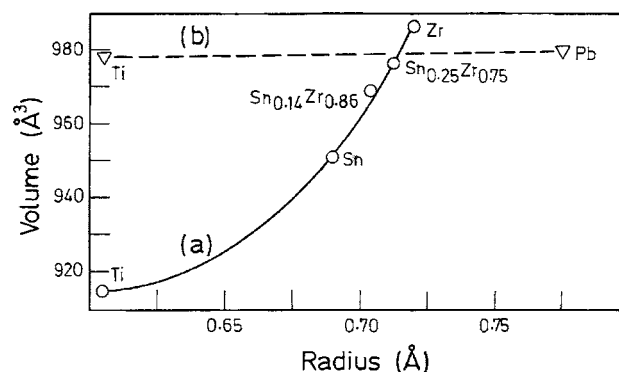

Fig. 3. Compounds with both (a) umbite- and (b) kostylevite-type structure: unit-cell volume vs. ionic radius in octahedral coordination.

only 0.1–0.3 meq g^{-1} in the pH range of 7–9, reaching a maximum of 1.6 meq g^{-1} at pH 12, where the precipitation of strontium hydroxide is to be expected. The experimental data for strontium can be explained by a blocking of channel entrances leading to the inner parts of the exchanger as a consequence of the exchange reaction not generating sufficient energy to overcome the hydration energy of the alkaline earth cation.

Since the chemical composition and the channel system of both phases are very similar, a question arises: why are their ion exchange properties different? The answer may lie in the flexibility of the framework and its capacity to adapt to counterion dimensions. Fig. 3a shows the cell volume of some potassium phases with umbite structure as a function of the average ionic radius of the hexa-coordinated cations.

The dimensions of the skeleton are a direct function of the tetravalent cation size, which demonstrates the capacity of adaptation from a tetrahedral sub-network to the dimensions of the hexa-coordinated ion. However, the substitution of titanium by lead in the kostylevite structure hardly alters cell volume. In this phase, the tetrahedral sub-network is very rigid and substantially determines the reticular parameter values.

The rigidity of the kostylevite-type structure compared with the flexibility of umbite is verified on determining the structural changes that accompany the dehydration process. In both cases, the water loss associated with the increase in temperature is a reversible process that begins immediately in the case of $K_2SnSi_3O_9 \cdot H_2O$ (Fig. 4a), while 150 °C must be exceeded for loss of mass to be detected
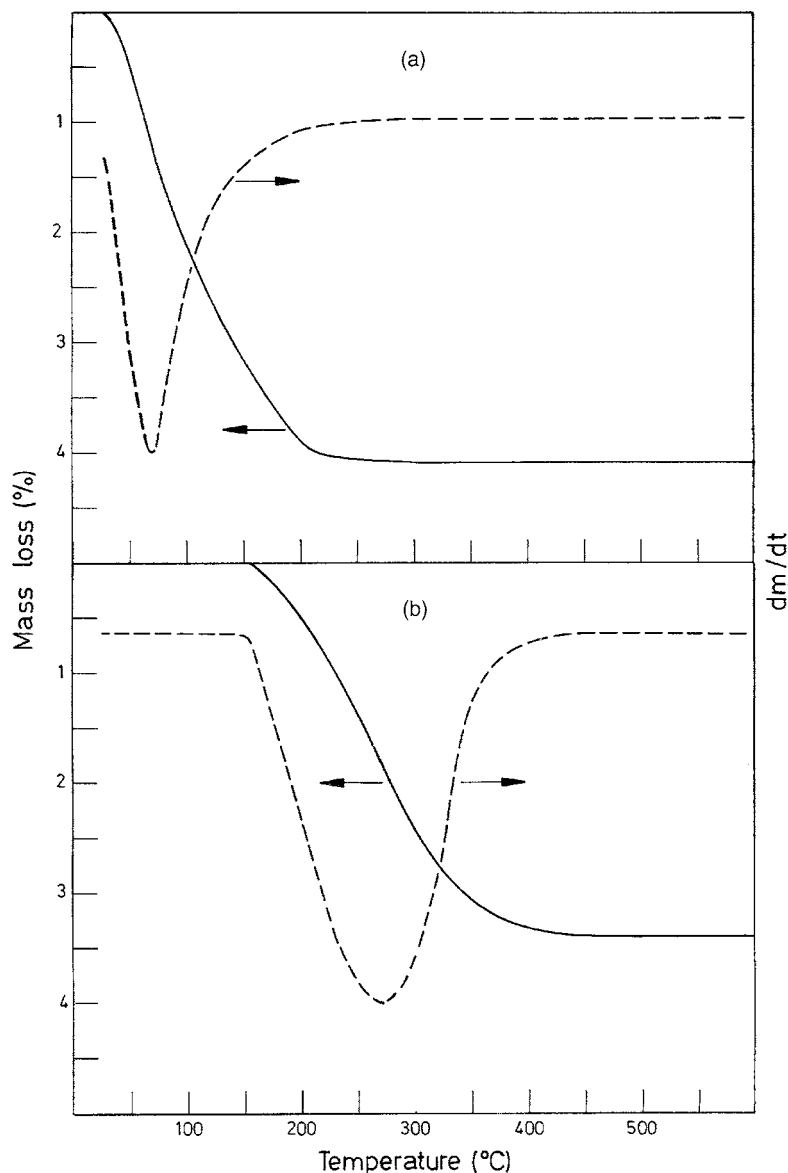
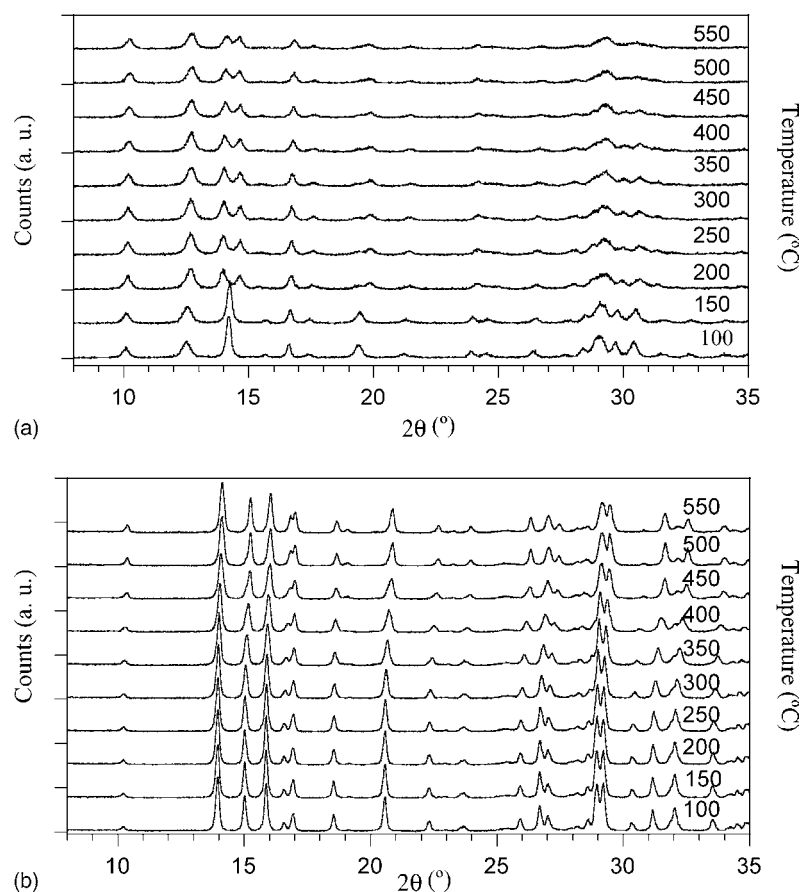Fig. 4. TG (—) and DTG (---) for (a) $K_2SnSi_3O_9 \cdot H_2O$ and (b) $K_2PbSi_3O_9 \cdot H_2O$.

Fig. 5. Temperature X-ray powder diffraction patterns from (a) $K_2SnSi_3O_9 \cdot nH_2O$ ($n \leq 1$) and (b) $K_2PbSi_3O_9 \cdot nH_2O$ ($n \leq 1$).

in $K_2PbSi_3O_9 \cdot H_2O$ (Fig. 4b). Thermodiffractometric data (Fig. 5) indicates that the semi-hydrated samples preserve the symmetry of the starting compound (Table 1). In both systems, the dehydration process takes place with cell volume reduction. The combination of dynamic and isothermal thermogravimetry (Fig. 6) allows us to ascertain the degree of hydration reached at each stabilization temperature. The unit-cell volume of the umbite-type flexible structure is a linear function of its water content (Fig. 7a). In contrast, when the hydration percentage is higher than 25%, the volume of the kostylevite-type rigid structure remains practically invariable (Fig. 7b). Subsequently, a

drastic decrease in both unit-cell volume and crystallinity is observed, finally obtaining an amorphous anhydrous compound. Table 2 shows that the anhydrous tin silicate crystallizes in a monoclinic cell, related to the orthorhombic cell of the monohydrated starting material. Although the unit-cell volume of $K_2SnSi_3O_9$ is practically invariant with temperature, contraction of the framework is observed in the *a*-axis direction, counteracted by expansion in the *c*-axis direction when the temperature increases.

In conclusion, the valuable properties of an inorganic ion exchanger are a function of its structural flexibility, in

Table 1
Unit-cell parameters of $K_2MSi_3O_9 \cdot nH_2O$ compounds

M	n	T (°C)	a	b	c	β	V
Sn	0.53	100	10.067(2)	13.095(3)	7.146(1)	–	942.1(3)
	0.32	150	10.032(2)	13.054(3)	7.129(2)	–	933.6(4)
Pb	1.00	100	6.5577(4)	11.7701(6)	13.0368(9)	103.573(4)	978.1(1)
	1.00	150	6.5575(4)	11.7701(6)	13.0372(6)	103.571(4)	978.2(1)
	0.64	200	6.5560(4)	11.7652(6)	13.0326(9)	103.563(4)	977.2(1)
	0.26	250	6.5523(4)	11.7515(7)	13.0998(9)	103.555(4)	974.6(1)
	0.16	300	6.5451(4)	11.7224(8)	12.995(1)	103.526(5)	969.4(1)
	0.07	350	6.5374(4)	11.6863(8)	12.956(1)	103.477(5)	962.5(1)
	0.00	400	6.5277(5)	11.640(1)	12.910(1)	103.408(6)	954.2(1)
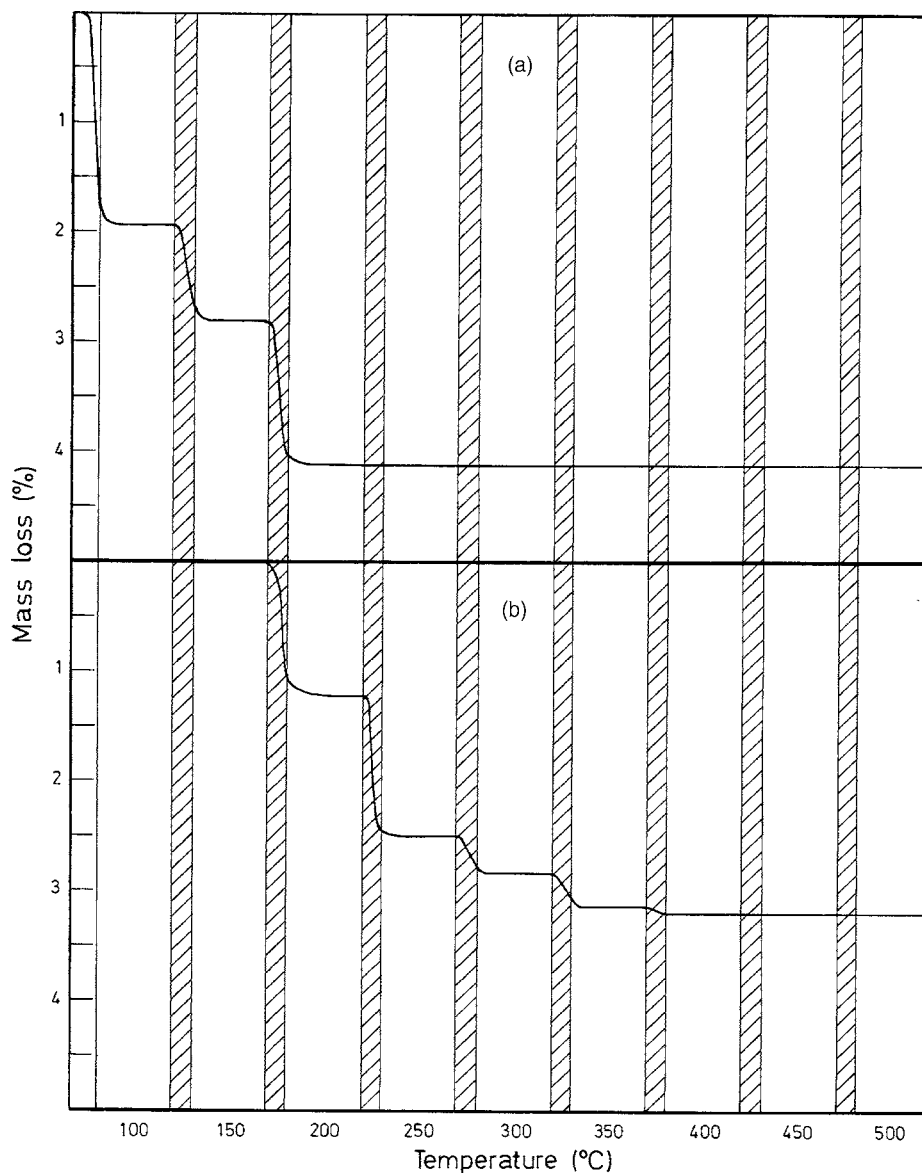
Fig. 6. Dynamic-isothermal TG curves of (a) $K_2SnSi_3O_9 \cdot H_2O$ and (b) $K_2PbSi_3O_9 \cdot H_2O$. In the non-dashed zone, the temperature remains constant and is equal to the corresponding abscissa value. In the zone between two constant temperatures (oblique lines), the rate of heating is $50\,^\circ C\,min^{-1}$.

Table 2
Unit-cell parameters of $K_2SnSi_3O_9$ as a function of temperature

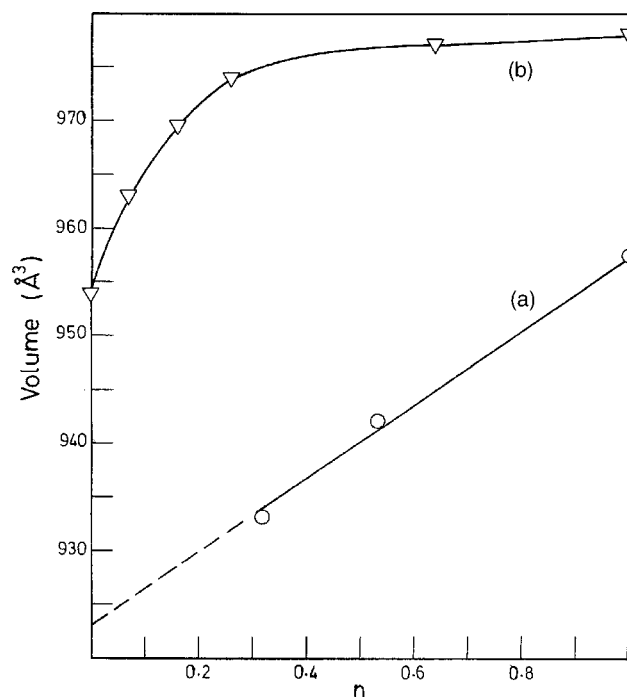| T (°C)	a	b	c	β	V
200	10.017(3)	12.932(4)	7.077(2)	92.56(2)	915.9(4)
250	10.016(3)	12.930(3)	7.078(2)	92.60(1)	915.9(4)
300	10.012(3)	12.932(3)	7.077(2)	92.54(1)	915.3(4)
350	10.001(3)	12.927(4)	7.077(2)	92.47(2)	914.1(4)
400	9.992(3)	12.932(4)	7.080(2)	92.37(1)	914.0(5)
450	9.995(3)	12.949(4)	7.088(2)	92.24(2)	916.7(5)
500	9.982(3)	12.932(4)	7.090(2)	92.08(2)	914.6(5)
550	9.972(4)	12.938(5)	7.089(2)	91.90(2)	914.1(6)

Fig. 7. Unit-cell volume vs. hydration degree: (a) $K_2SnSi_3O_9 \cdot nH_2O$ and (b) $K_2PbSi_3O_9 \cdot nH_2O$.

addition to its chemical composition, intracrystalline porosity and surface characteristics.

Acknowledgements

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