New family of silicate phases with the pollucite structure

Leticia M. Torres-Martinez and A. R. West

University of Aberdeen, Department of Chemistry,
Meston Walk, Old Aberdeen AB9 2UE, Scotland, United Kingdom

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Abstract. A new family of silicate phases, $Cs_2MSi_5O_{12}$: M = Be, Mg, Fe, Co, Ni, Zn, Cd; $Rb_2MSi_5O_{12}$: M = Mg, Fe, (Co, Zn) has been prepared with the cubic pollucite structure, a in the range 13.3 to 13.8 Å, space group $Ia3d$, $Z = 8$. The structure of one, $Rb_2MgSi_5O_{12}$, has been refined to $R = 10.8\%$ using X-ray powder data. The structures are built of a 3D, $[MSi_5O_{12}]^{2-}$ framework containing large, 12-coordinated cavities for the alkali cations. These structures are unusual in that a wide range of divalent cations have partially replaced Si^{4+} in the silicate anion framework.

Introduction

Pollucite, $CsAlSi_2O_6$, is a framework aluminosilicate containing large, 12-coordinated cavities suitable for occupation by Cs^+ ions (Strunz, 1936; Naray-Szabo, 1938; Newnham, 1967). The unit cell is cubic with space group $Ia3d$, $Z = 16$. Similar alumino-silicate frameworks are present in analcite, $NaAlSi_2O_6 \cdot H_2O$ and leucite, $KAlSi_2O_6$ (Taylor, 1938; Beattie, 1954; Knowles et al., 1965; Wyart, 1941; Deer et al., 1963; Wyckoff, 1968), although leucite is tetragonal below 605° (Wyart, 1941; Deer et al., 1963; Wyckoff, 1968).

   Structural studies on these phases are complicated by the occurrence of twinning in tetragonal leucite (Mazzi et al., 1976) and by Si, Al disorder in the aluminosilicate framework. Various analogues of pollucite and leucite, containing other trivalent ions instead of Al^{3+} have been reported: Fe-pollucite, $CsFeSi_2O_6$ (Kopp et al., 1963; Kume and Koizumi, 1965), Fe-

leucite, $KFeSi_2O_6$, tetragonal $RbFeSi_2O_6$ (Hirao et al., 1976) and tetragonal $RbAlSi_2O_6$ (Hirao et al., 1976; Barrer et al., 1953; Taylor and Henderson, 1968). Recently, we have synthesised $Cs_2BeSi_5O_{12}$ (Torres-Martinez et al., 1984) with the pollucite structure. It seemed likely that a variety of other divalent ions should also enter the pollucite framework; this was found to be the case and these results are reported here.

Experimental

Starting materials were SiO_2 (high purity, crushed quartz), Cs_2CO_3 (Aldrich, 99.9% pure), Rb_2CO_3 (Fluka, 98% pure), MgO (Hopkin and Williams, Analar), $Fe(COO)_2$, $CoCO_3$, $NiCO_3$, ZnO, CdO (all BDH, reagent grade). Mixtures in the stoichiometric ratio, $(M_2^+CO_3:M^{2+}O:5\,SiO_2$ with $M^+ = Rb, Cs; M^{2+} = Mg, Zn$ etc. were prepared in ~ 10 g quantities by mixing into a paste with acetone, drying and firing in Pt crucibles or foil boats, initially at 600 to 700°C to expel CO_2 and finally at 900 to 1200°C for 1 to 3 days, depending on composition, to complete the reaction. Some samples were melted, quenched to form a glass, and subsequently crystallised at temperatures in the range 900 to 1200°C. The products were identified by X-ray powder diffraction using a Hägg Guinier focusing camera, $CuK\alpha_1$ radiation. For accurate d-spacing measurements, analar grade KCl, $a = 6.2931$ Å, was added as an internal standard and the films were measured using a Cooksley microdensitometer. The powder patterns were indexed by comparison with that of $Cs_2BeSi_5O_{12}$ (Torres-Martinez et al., 1984) and unit-cell dimensions obtained by least-squares refinement.

Powder intensities suitable for a structure determination were obtained using a Philips diffractometer, $CuK\alpha$ radiation, with a slow scan speed of $\frac{1}{2}°$ min^{-1}. Intensities, measured from the diffractometer chart by using the method of counting squares to give peak areas, were corrected for Lp factors and multiplicities in the usual way. Structure refinement was carried out with a least-squares program using F_{hkl} values.

Melting points were determined by placing powdered samples, wrapped in Pt foil, in a vertical tube furnace whose temperature was controlled and measured to ±5°C. The samples were heated for short times, $\sim \frac{1}{2}$ h, quenched into Hg and their X-ray powder patterns recorded. The liquids that formed on melting most of the new phases readily formed glasses on cooling to room temperature. It was therefore an easy matter to determine whether or not melting had occurred from the presence (not melted) or absence (melted) of lines in the X-ray powder patterns of the quenched samples.

Several of the phases were found to exhibit polymorphism. This was shown by heating samples at selected temperatures followed by either quenching or slowly cooling to room temperature.

Results and discussion

Ten new silicate phases of general formula $M_2^+M^{2+}Si_5O_{12}$ with the pollucite structure have been synthesised. They were prepared either by solid state reaction or by crystallisation of glass or by both methods. All are thermodynamically stable and melt congruently at high temperatures. Some are stable only at high temperatures and transform to other polymorphs on cooling. Crystallographic data, melting points, conditions of synthesis and polymorphism of the new phases, together with data for $Cs_2BeSi_5O_{12}$ (Torres-Martinez et al., 1984) are given in Table 1.

The new, pollucite-like phases, labelled α phases, are cubic with space group $Ia3d$. For two of them, $Cs_2CoSi_5O_{12}$ and $Rb_2MgSi_5O_{12}$, the space group was confirmed using selected area electron diffraction. Indexed X-ray powder data for $Rb_2MgSi_5O_{12}$ are given in Table 2; data for the remainder have been submitted to the JCPDS X-ray powder diffraction file.

The structure of one of the new phases, $Rb_2MgSi_5O_{12}$, was confirmed by least-squares refinement of the observed structure factors, F_{hkl}, using as starting coordinates, the refined parameters of $Cs_2BeSi_5O_{12}$ (Torres-Martinez et al., 1984). Initially, 18 uniquely indexed reflections were used in the refinement and an R value of 10.1% obtained. Subsequently, an additional 4 overlapping reflections were included. Assignment of intensities to the component peaks was made using the calculated structure factors as a guide. After the final refinement using a total of 27 reflections, an R value of 10.8% was obtained. For the final refinement, all relevant positional coordinates and the isotropic temperature factors were allowed to refine independently. The relevant data are given in Table 2 with final atomic coordinates in Table 3 and a selection of bond distances and angles in Table 4.

The structure of $Rb_2MgSi_5O_{12}$ is essentially the same as that of pollucite, $CsAlSi_2O_6$ (Strunz, 1936; Náray-Szabó, 1938; Newnham, 1967) and $Cs_2BeSi_5O_{12}$ (Torres-Martinez et al., 1984). It may be described as a 3 D magnesiosilicate framework built of corner-sharing $(Mg,Si)O_4$ tetrahedra with the large Rb^+ ions in 12-coordinate cavities. There was no evidence of ordering of Mg and Si over the 48 (g) sites.

A comparison of $Cs_2BeSi_5O_{12}$ and $Rb_2MgSi_5O_{12}$ shows that, while $Rb_2MgSi_5O_{12}$ has the larger unit-cell dimension, six of the Rb—O bonds in it are shorter than the corresponding six Cs—O bonds in $Cs_2BeSi_5O_{12}$. There appear to be two factors involved in this effect. First, introduction of Mg in place of Be in the anion framework causes a small, average increase in the (M^{2+},Si^{4+})—O bond lengths. Second, the anion framework becomes slightly distorted so as to allow six shorter Rb—O bonds.

The temperature factors given for $Rb_2MgSi_5O_{12}$, Table 3, are all rather large. This may be variously attributed to (a) the limited data set used (b)

Table 1. Properties of new polucite-like phases

Phase	Conditions of synthesis (α polymorph)	Other polymorphs, conditions of synthesis	$a(\text{Å})$	Melting point, °C
$Cs_2BeSi_5O_{12}$	crystallisation of glass 900°C or solid state reaction, 1000–1200°C	—	13.406(1)	1420 ± 20
$Cs_2MgSi_5O_{12}$	crystallisation of glass 900°C or solid state reaction, 1400°C	γ, solid state reaction at 1000–1200°C	13.695(1)	1450 ± 20
$Cs_2FeSi_5O_{12}$	solid state reaction, 1100°C	—	13.834(2)	1420 ± 30
$Cs_2CoSi_5O_{12}$	crystallisation of glass 1100°C	γ(or δ), solid state reaction 1000–1200°C	13.672(1)	1340 ± 20
$Cs_2NiSi_5O_{12}$	1300°C, quench	δ(or γ), 1200°C	13.654(1)	1325 ± 50
$Cs_2ZnSi_5O_{12}$	crystallisation of glass 900°C; 1380°C, quench	δ(or γ), 1100–1300°C	13.662(2)	1400 ± 20
$Cs_2CdSi_5O_{12}$	solid state reaction, 1000°C	—	13.791(2)	1090 ± 20
$Rb_2MgSi_5O_{12}$	1350°C, solid state reaction	η, non-cubic 1100–1300°C	13.530(1)	1360 ± 40
$Rb_2FeSi_5O_{12}$	crystallisation of glass 1000°C	—	13.650(4)	1070 ± 20
$Rb_2CoSi_5O_{12}$*	1250°C, quench*	η, non-cubic 1100–1200°C		1260 ± 10
$Rb_2ZnSi_5O_{12}$+	1300°C, quench*	η, non-cubic 1100–1200°C		1325 ± 20

* It was not possible to obtain a pure α polymorph; partial transformation to η occurred, even on rapid quenching

+ It was not possible to obtain a pure α polymorph free from one or two weak extra lines which could be associated with either γ or η polymorphs

Table 2. X-ray powder data for $Rb_2MgSi_5O_{12}$. $a = 13.530 \pm 0.001\,\text{Å}$, S.G. $Ia3d$

hkl	d_{obs} (Å)	d_{calc}(Å)	I_{obs}	F_{obs}	F_{calc}
022	4.805	4.784	1.7	6.3	9.9
123	3.623	3.616	24.7	16.2	18.5
004	3.387	3.383	100	99.3	96.6
024	3.029	3.026	3.8	11.0	9.7
233	2.887	2.885	38.0	36.4	35.4
134	2.656	2.654	4.9	10.1	10.8
125	2.472	2.470	1.4	6.0	6.1
044	2.3921	2.3918	18.6	44.5	47.1
116 } 235 }	2.1949	2.1949	7.7	4.8 / 15.4	4.8 / 16.5
136	1.9945	1.9949	3.9	12.5	12.6
444	1.9535	1.9529	2.6	25.7	20.6
345	1.9133	1.9135	0.9	6.3	4.6
046	1.8772	1.8763	1.0	9.9	12.9
127 } 255 } 336 }	1.8411	1.8412	8.7	14.4 / 8.7 / 19.2	15.0 / 9.4 / 20.8
237 } 156 }	1.7180	1.7184	9.5	23.2 / 3.9	27.8 / 4.6
008	1.6910	1.6913	3.0	38.3	35.8
147	1.6656	1.6655	2.5	12.5	10.5
028	1.6409	1.6408	1.9	15.7	11.5
356	1.6163	1.6172	2.0	11.6	7.8
138 } 347 }	1.5729	1.5729	2.2	12.2 / 3.1	11.4 / 2.8
257	1.5317	1.5320	1.6	11.2	11.8
048	1.5129	1.5127	2.3	19.3	18.6

Table 3. Atomic parameters for $Rb_2MgSi_5O_{12}$

Atom	Position	x	y	z	B_{iso}
O	96 h	0.100 ± 0.001	0.127 ± 0.002	0.717 ± 0.001	4.0
Si, Mg	48 g	0.125	0.665 ± 0.001	0.585 ± 0.001	2.3
Rb	16 b	0.125	0.125	0.125	6.0

Table 4. Some bond distances and angles

(Mg,Si)−O	$1.610 \pm 0.022\,\text{Å}$ ($2\times$)
	$1.628 \pm 0.019\,\text{Å}$ ($2\times$)
Rb−O	$3.598 \pm 0.018\,\text{Å}$ ($6\times$)
	$3.291 \pm 0.018\,\text{Å}$ ($6\times$)
O−(Mg,Si)−O	$104.7 \quad \pm 1.1^\circ$
	$118.7 \quad \pm 1.1^\circ$ ($2\times$)
	$106.9 \quad \pm 1.1^\circ$ ($2\times$)
	$101.8 \quad \pm 1.1^\circ$

disorder in oxygen positions, associated with different sizes of the randomly arranged MgO_4, SiO_4 tetrahedra (c) disorder in Mg, Si positions and (d) the rather long Rb−O bond lengths and therefore, large vibration amplitudes for Rb. Further evidence of disorder in the structure is indicated by the distorted average shape of the (Mg,Si)O_4 tetrahedra in which the bond angles vary from 102 to 119°. In $Cs_2BeSi_5O_{12}$, by comparison, the bond angles were all between 104 and 113°. In summary, therefore, it is considered that the atomic coordinates given in Table 3 represent an average structure and that on a microscopic scale, considerable structural distortion and disorder is likely to be present.

Variations in lattice parameters, a, between the different phases reported in Table 1 are in approximate accord with the relative sizes of the component M^+, M^{2+} ions. Thus, for the Cs^+ phases the lattice parameter of the transition metal ion-containing phases gradually decreases from M = Fe to Zn; the sizes of the Mg, Zn-containing phases are approximately equal. Further, for a given M^{2+} ion, the lattice parameter of a Cs^+ phase is larger than that of the Rb^+ phase. However, all of the lattice parameter values given in Table 1 fall within a span of only $\sim 3\%$ which is much smaller than the spread in the radii of either the M^+ or M^{2+} ions that are present. This indicates that the lattice parameter value is controlled primarily by the size of the silicate anion framework. The latter is modified to a small degree by the various divalent ions that substitute into the framework and by the different alkali cations that occupy the large, 12-coordinate cavities.

Several of the new phases are polymorphic, as given in Table 1. The polymorphs fall into two main categories. The γ, δ polymorphs are cubic, like the α polymorphs, but show extra weak lines in their X-ray powder patterns. The δ polymorphs have a primitive cubic space group with no systematic absences, as shown for the structurally related germanate phases, $Cs_2ZnGe_5O_{12}$, $Cs_2CoGe_5O_{12}$ and $Rb_2MgGe_5O_{12}$ (Torres-Martinez et al., 1984). The γ polymorphs are primitive cubic but have systematic absences associated with a single a glide plane and probable space group $Pa3$ (Torres-Martinez et al.). In some of the phases it was not possible to distinguish from powder data alone between δ and γ polymorphs. The lattice constants of the δ, γ polymorphs were not determined but, in each case, appeared to be very similar to those of the parent α polymorphs.

The η polymorphs are non-cubic and are characterised by split lines in their X-ray powder patterns in comparison with the α polymorphs. The η polymorphs are not simply tetragonal, leucite-like phases (Torres-Martinez et al.) although the related phase, $Rb_2BeSi_5O_{12}$ (labelled ε) is leucite-like (Torres-Martinez et al., 1984). The η polymorphs appear to have symmetry lower than tetragonal (Torres-Martinez et al.).

It also appears to be generally the case that in those phases that show polymorphism, the α, pollucite-like polymorph is stable at high tempera-

tures and the γ, δ and η polymorphs are stable at lower temperatures. The transitions between α and γ, δ or η polymorphs were generally found to be reversible.

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