JOURNAL OF SOLID STATE CHEMISTRY 53, 354–359 (1984)

Synthesis and Structure of a New Family of Phases, $A_2MGe_5O_{12}$: A = Rb, Cs; M = Be, Mg, Co, Zn

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Received September 12, 1983; in revised form December 9, 1983

A new family of eight germanate phases, $A_2MGe_5O_{12}$: A = Rb, Cs; M = Be, Mg, Co, Zn, has been synthesized. They are cubic with a in the range 13.7 to 14.0 Å, $Z = 8$, and space group $I\bar{4}3d$. These phases, named the β phases, are isostructural with $KBSi_2O_6$ which has a structure related to that of pollucite, $CsAlSi_2O_6$. The structure of one, $Rb_2ZnGe_5O_{12}$, has been refined to an R value of 0.079 using X-ray powder diffraction data. Several of the new phases are polymorphic. $Cs_2ZnGe_5O_{12}$, $Cs_2CoGe_5O_{12}$, and $Rb_2MgGe_5O_{12}$ form low-temperature, δ polymorphs which have primitive cubic unit cells. $Rb_2ZnGe_5O_{12}$ forms a low-temperature, ε polymorph which is probably a tetragonal distortion of the β structure.

Introduction

During a study of complex oxide phases containing Rb, Cs, we have recently prepared the new phase $Cs_2BeSi_5O_{12}$ (*1*). It has the same crystal structure as pollucite, $CsAlSi_2O_6$ (*2–4*), with space group $Ia3d$ and may be regarded as derived from pollucite via the replacement mechanism:

$$2Al^{3+} \rightleftharpoons Be^{2+} + Si^{4+}$$

In the structure of $Cs_2BeSi_5O_{12}$, the Be and Si atoms appear to be disordered over the 48 g sites. These sites belong to tetrahedra which link up, by corner-sharing, to form a 3D framework. The large Cs^+ cations are located within 12 coordinate cavities in the beryllosilicate framework.

We now report the synthesis of a new family of germanate phases. Although these are similar structurally, to $Cs_2BeSi_5O_{12}$, they have a different space group, $I\bar{4}3d$ and are better regarded as derived from the structure of $KBSi_2O_6$ (*5*).

Experimental

Starting materials were GeO_2 (electronic grade), Rb_2CO_3 (Fluka, 98% pure), Cs_2CO_3 (Aldrich, 99.9% pure), ZnO (BDH, Lab. reagent), MgO (Hopkin and Williams, Analar), BeO (Aldrich), and $CoCO_3$ (BDH, Lab. reagent). Mixtures in the stoichiometric ratio, $(Rb, Cs)_2CO_3 \cdot (Be,Zn,Co,Mg)O \cdot 5\,GeO_2$ were prepared in ~10-g quantities by mixing into a paste with acetone, drying, and firing in Pt crucibles, initially at 600 to 700°C to expel CO_2 and finally at 900–1100°C for 1–3 days to complete the reaction. The products were identified by X-ray powder diffraction using a Hägg Guinier focusing camera, $CuK\alpha_1$ radiation. For accurate d-spacing measurements, KCl (a = 6.2931 Å) was added as an internal stan-

0022-4596/84 $3.00

dard. Powder intensities suitable for crystal structure determination were obtained using a Philips diffractometer, CuKα radiation, with a slow-scan speed, $\frac{1}{2}°2\theta$ min^{-1}. Intensities were corrected for Lp factors and multiplicities in the usual way. Structure refinements were carried out with a least squares program (*6*) 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 $\sim\frac{1}{2}$ hr, quenched into Hg and analysed with the Hägg Guinier X-ray camera. Since the liquids that formed on melting all of the new phases readily gave glasses on quenching, it was an easy matter to determine whether or not melting had occurred from the presence or absence of lines in the powder X-ray patterns of quenched samples.

Polymorphism of the new phases was studied by heating samples for prolonged periods at different temperatures or by subjecting samples to a slow cool from high temperatures.

Unit cell and space group information was obtained by selected area electron diffraction using an AEI 803 microscope fitted with a 60° double-tilt specimen stage.

Results

Synthesis of the New "β" Phases, Unit Cell, and X-Ray Powder Data

Following on from the synthesis of $Cs_2BeSi_5O_{12}$ (*1*) with a pollucite structure, various other combinations of oxides of mono-, di-, and tetravalent ions have been tried in order to synthesize possible other new phases. A new family of phases, named the β phases, has been prepared which so far contains eight members, $A_2MGe_5O_{12}$: A = Rb, Cs; M = Be, Mg, Co, Zn. These phases were all readily synthesized by solid state reaction at ~1000°C, apart from $Rb_2CoGe_5O_{12}$ which was prepared by crystallizing glass of the same composition, at ~900°C. The X-ray powder data of these new phases are similar to those of $Cs_2BeSi_5O_{12}$ but contain an extra set of lines, as shown in Fig. 1b. Some of the extra lines are due to the absence of the *a* glide plane, present in $Cs_2BeSi_5O_{12}$, space group *Ia*3*d*.

Selected area electron diffraction of a selection of β phases showed them all to have a cubic unit cell with the conditions for reflection hkl: $h + k + l = 2n$; hhl: $2h + l = 4n$. These absences indicated a body-centered lattice with a *d* glide plane. A search through the International Tables for Crystallography (*7*) showed the space group to be $I\bar{4}3d$ (No. 220). The unit cells obtained by electron diffraction enabled the X-ray powder patterns to be indexed and accurate cell dimensions were obtained by least-squares refinement. Unit cell data are given in Table I and indexed powder X-ray data in Table II.[1] Also included in Table I are melting points and densities of the new phases. Experimental density data for one phase confirmed the unit cell contents, *Z*, to be 8 formula units.

Crystal Structure of the β Phases: $Rb_2ZnGe_5O_{12}$

From a comparison of unit cell and space group data for the β phases with that of $KBSi_2O_6$ (*5*), it seemed likely that $KBSi_2O_6$ and the β phases were isostructural. In order to confirm this, X-ray powder intensity data for one β phase, $Rb_2ZnGe_5O_{12}$, were collected. Oxygen atoms were placed in two sets of 48(e) positions, rubidium in 16(c) positions and zinc, germanium at random in 48(e) positions. Starting coordinates were taken as those for $KBSi_2O_6$ (*5*). For the initial refinement of the positional coordinates and isotropic temperature factors,

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[1] Submitted to the X-ray powder diffraction file. Copies available from the authors on request.

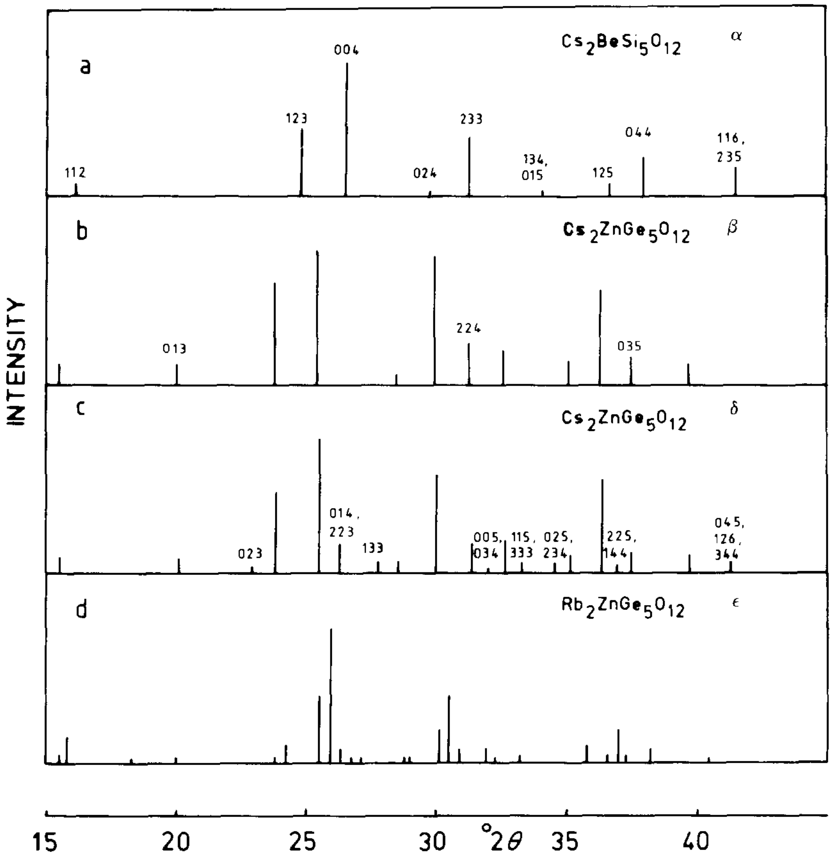

FIGURE 1

26 uniquely indexed lines were used. Subsequently, an additional 18 peaks were added, each of which was composed of two or more overlapping lines. For these, the intensities of the component peaks were estimated according to the calculated *F* val-

TABLE I

UNIT CELL DATA, MELTING POINTS, AND DENSITIES OF β PHASES

β-Phase	*a* (Å)	m.p. (°C)	Calculated density (g/cm^3)	Experimental density (g/cm^3)
$Cs_2BeGe_5O_{12}$	13.7245 ± 0.0008	1160 ± 30	4.26	
$Cs_2MgGe_5O_{12}$	13.9748 ± 0.0006	1280 ± 30	4.11	
$Cs_2ZnGe_5O_{12}$	13.9985 ± 0.0005	1140 ± 30	4.29	
$Cs_2CoGe_5O_{12}$	14.0021 ± 0.0008	1180 ± 20	4.26	
$Rb_2BeGe_5O_{12}$	13.4728 ± 0.0007	1120 ± 20	3.99	4.01
$Rb_2MgGe_5O_{12}$	13.7826 ± 0.0007	1000 ± 20	3.81	
$Rb_2ZnGe_5O_{12}$	13.7374 ± 0.0008	960 ± 20	4.05	
$Rb_2CoGe_5O_{12}$	13.7307 ± 0.0008	960 ± 20	4.03	

[a] Measured by displacement of toluene in a S.G. bottle.

TABLE III

ATOMIC PARAMETERS FOR β-$Rb_2ZnGe_5O_{12}$

Atom	Position	X	Y	Z	B_{iso}
O(1)	48e	0.252 ± 0.002	0.160 ± 0.002	0.357 ± 0.002	2.6
O(2)	48e	0.123 ± 0.002	0.286 ± 0.001	0.437 ± 0.001	0.7
Zn, Ge	48e	0.1267 ± 0.0005	0.1709 ± 0.0003	0.4078 ± 0.0003	2.7
Rb	16c	0.1130 ± 0.0005	0.1130 ± 0.0004	0.1130 ± 0.0005	2.2

ues. A total of 70 reflections were used for the final refinement, which gave an R-value of 0.079 and the atomic coordinates listed in Table III. X-ray powder data for $Rb_2ZnGe_5O_{12}$, including observed and calculated F values, are given in Table IV. A selection of the more important bond lengths and angles is given in Table V.

The essential features of the structure of $Rb_2ZnGe_5O_{12}$ are clear. It has a framework built of corner-sharing $(Zn,Ge)O_4$ tetrahedra which link up to form four- and six-membered rings. Rubidium atoms occupy large cavities within this framework. As such, the structure is rather similar to that of $Cs_2BeSi_5O_{12}$ and pollucite (*1–4*). Both structure types have a similar framework but the absence of the *a* glide plane in $Rb_2ZnGe_5O_{12}$ and the β phases allows the framework to adopt a more flexible configuration. The results of the structural refinement obtained for $Rb_2ZnGe_5O_{12}$, Tables III and V cannot be regarded as entirely satisfactory and complete, however. Although the R-factor has a reasonable value, the shapes of the $(Zn,Ge)O_4$ tetrahedra appear to be rather distorted with one particularly short bond length of 1.63 Å. Clearly, some disorder is present in the structure, associated with the random distribution of Zn and Ge over the tetrahedral sites. Differences in size and/or shape of individual ZnO_4, GeO_4 tetrahedra will therefore lead to some disorder in the positions of the oxygen atoms and this is reflected in the distorted shape of the average $(Zn,Ge)O_4$ tetrahedron, Table V. It may be that, on a unit cell scale, the true symmetry of $Rb_2ZnGe_5O_{12}$ is lower than cubic, although there is no direct evidence, from the electron diffraction results, to support this.

Polymorphism

All eight of the new phases give, under normal conditions of solid state reaction at, e.g., 1000°C followed by fairly rapid cooling (~2 to 5 min) to room temperature, a β phase with space group $I\bar{4}3d$. However, on slowly cooling samples, from, e.g., 900 to 400°C over a period of 5 days, some of the phases undergo a polymorphic transformation. Two types of behavior have been observed. First, the X-ray powder patterns of three phases, $Cs_2ZnGe_5O_{12}$, $Cs_2CoGe_5O_{12}$, and $Rb_2MgGe_5O_{12}$ show the presence of a set of weak extra lines, Fig. 1c. From electron diffraction analyses, a cubic unit cell was again indicated but there appeared to be no systematic absences. Hence, both the body centering and the *d* glide plane of the β phases is destroyed in these low-temperature polymorphs, which have been labeled δ. Indexed X-ray powder data for one δ phase are given in Table VI.[1] the reverse transformation $\delta \rightarrow \beta$, was studied briefly by heating samples of δ phases at constant temperature followed by quenching to room temperature. For all three cases the $\delta \rightarrow \beta$ transformation took place in the range 700 to 900°C.

The second type of polymorphic behavior was observed in $Rb_2ZnGe_5O_{12}$ and is characterized by the doubling of certain lines in the X-ray powder pattern (Fig. 1d).

TABLE IV

X-Ray Data for β-$Rb_2ZnGe_5O_{12}$

hkl	d_{OBS} (Å)	d_{CALC} (Å)	I_{OBS}	F_{OBS}	F_{CALC}
112	5.632	5.608	18.7	18.2	22.4
022	4.872	4.857	1.2	7.6	7.5
013	4.344	4.344	2.3	8.3	11.7
123	3.682	3.672	14.4	17.6	19.1
004	3.443	3.434	100.0	141.1	143.0
024	3.079	3.072	4.4	16.8	17.4
233	2.934	2.929	50.0	59.3	62.0
224	2.808	2.804	10.6	28.6	23.4
015	2.700	2.694	5.5	49.5	51.7
134				14.9	16.8
125	2.512	2.508	13.0	25.4	25.8
044	2.432	2.429	27.2	76.3	74.6
035	2.358	2.356	10.6	34.8	29.6
116	2.2285	2.2285	2.4	16.1	20.3
235				4.9	5.6
145	2.1204	2.1197	1.7	11.2	8.9
136	2.0269	2.0255	16.1	36.2	29.1
444	1.9842	1.9828	3.8	44.3	47.6
017	1.9435	1.9428	5.8	13.8	12.9
345				20.6	20.4
046	1.9060	1.9050	1.2	14.8	13.7
127	1.8700	1.8694	16.1	19.5	18.5
255				21.1	19.5
336				44.4	42.9
246	1.8363	1.8357	3.8	19.8	20.9
037	1.8038	1.8038	0.9	14.3	14.5
156	1.7449	1.7447	16.1	54.5	65.1
237				43.1	45.6
008	1.7177	1.7172	1.8	42.1	40.6
147	1.6909	1.6910	6.0	27.6	28.0
028	1.6660	1.6659	2.5	25.4	26.9
066	1.6197	1.6190	2.3	23.0	22.1
228				19.4	20.8
138	1.5967	1.5969	6.7	15.2	16.3
057				23.5	24.4
347				21.5	21.1
048	1.5363	1.5359	1.4	21.6	21.5
248	1.4987	1.4989	1.6	16.4	14.7
556	1.4811	1.4813	3.8	4.4	5.3
129				16.4	17.8
167				19.8	20.2
466	1.4646	1.4644	1.7	25.0	27.9
039	1.4479	1.4480	4.8	10.2	10.3
457				28.4	28.6
158				6.1	6.8
239	1.4167	1.4169	4.9	14.4	13.6
367				27.4	28.5
448	1.4021	1.4021	0.9	18.8	19.9
358	1.3875	1.3877	2.9	21.9	19.6
149				10.7	10.5
068	1.3734	1.3737	2.0	29.1	28.9
277	1.3598	1.3602	5.5	26.5	28.5
1110				41.0	42.9
0210	1.3471	1.3471	1.1	3.5	3.5
268				15.1	18.0
567	1.3095	1.3098	4.5	3.6	3.9
259				2.1	2.8
1310				32.1	35.0
178	1.2866	1.2866	2.7	25.8	28.5
468	1.2753	1.2755	1.4	18.9	17.9
0410				3.7	3.2
169	1.2645	1.2646	1.9	3.0	3.2
3310				30.7	31.3
369	1.2237	1.2238	4.7	10.6	7.7
1510				33.3	24.7
1211				5.9	4.3
279	1.1864	1.1867	1.5	7.6	7.6
677				11.9	13.6
2311				10.9	11.7
3510				13.5	14.9

This doubling may be associated with a tetragonal distortion of the high-temperature, cubic $Rb_2ZnGe_5O_{12}$ structure, although electron diffraction or single crystal X-ray diffraction work is needed to check this.

The structures of the δ polymorphs and the non-cubic ε polymorph of $Rb_2ZnGe_5O_{12}$ are not known. However, from the similarity of their powder patterns to those of the parent β phases, it seems highly likely that they are distorted variants of the β structure. Probably, these distortions involve some twisting or buckling of the structural framework of linked tetrahedra.

It is perhaps significant that those phases which undergo polymorphic transformations on slow cooling are those that have the largest unit cell dimensions in their respective groups of Rb and Cs phases. These phases may have slightly more open structures, more flexibility in their structural frameworks and therefore, the ability to contract on cooling by means of a structural distortion. The concepts of "expanded"

TABLE V

SOME BOND DISTANCES AND ANGLES IN β-$Rb_2ZnGe_5O_{12}$

(Zn,Ge)–O	1.86 ± 0.03 Å	O–(Zn,Ge)–O	101.4 ± 1.1
	1.69 ± 0.03 Å		111.8 ± 1.1
	1.63 ± 0.02 Å		109.1 ± 1.0
	1.90 ± 0.02 Å		116.9 ± 1.1
			117.0 ± 1.0
			100.0 ± 1.1
Rb–O	3.91 ± 0.02 Å (6 ×)		
	3.18 ± 0.03 Å (6 ×)		

and "collapsed" networks, proposed by Henderson and Taylor (*8*) and applied by them to other framework structures, may be applicable to the present structures.

Acknowledgments

We thank R. Alan Howie for advice with the computer programs and the Computer Centre, University of Aberdeen for the use of facilities. L. M. T-M thanks CONACYT, Mexico, for a scholarship.

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