

Synthesis of aenigmatite

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SUMMARY. Aenigmatite with the formula $\text{Na}_4[\text{Fe}_{10}^{2+}\text{Ti}_2]\text{Si}_{12}\text{O}_{40}$ has been synthesized hydrothermally, at 700 °C and 1000 bars $P_{\text{H}_2\text{O}}$, from an oxide starting material. The oxygen fugacity was controlled by means of an iron-wüstite buffer. An indexed X-ray powder pattern of synthetic aenigmatite is given, together with comparative data on two natural samples. One of the aenigmatites, from Kola, U.S.S.R., is known to be triclinic (Kelsey and McKie, 1964). The powder patterns of this and the synthetic aenigmatite are so similar that it is concluded that the latter is also triclinic, at least at room temperature.

AENIGMATITE (cosyrite) is a fairly common constituent of sodium-rich peralkaline igneous rocks. The unit cell of aenigmatite was recently determined by Kelsey and McKie (1964), who also surveyed the available chemical analyses. They found that modern analyses did not vary greatly, and suggested an idealized formula of $\text{Na}_4[\text{Fe}_{10}^{2+}\text{Ti}_2]\text{Si}_{12}\text{O}_{40}$. Ernst (1962) synthesized a titanium-free 'aenigmatite' during the course of a study of alkali amphibole stability relations, using the bulk composition $\text{Na}_2\text{O} \cdot 5\text{FeO}_x \cdot 8\text{SiO}_2 + \text{excess H}_2\text{O}$. An X-ray powder diffractometer trace of this mineral gave similar d -spacings for principal peaks to those of a naturally occurring aenigmatite (U.S.N.M. 95499) from Julianchaat, Greenland. The titanium-free 'aenigmatite' had a rather limited stability field in terms of pressure (< 900 bars $P_{\text{H}_2\text{O}}$), temperature (maximum range of 650–800 °C at low $P_{\text{H}_2\text{O}}$), and oxygen fugacity (lower than produced by a fayalite-(magnetite+quartz) buffer).

This note reports the synthesis of titaniferous aenigmatite with a formula corresponding to that suggested by Kelsey and McKie. The starting material was a combined 'gel' and oxide mix. The Na_2O , FeO , and SiO_2 were first combined as a 'gel', using methods recently described by Hamilton and Henderson (1968). Then the appropriate amount of Specpure TiO_2 was mixed into the fired 'gel' by prolonged grinding in an agate mortar.

Charges of 'gel'+oxide were sealed, together with excess water, in tubes of silver/palladium ($\text{Ag}_{70}/\text{Pd}_{30}$) alloy. These were placed, surrounded by a buffer of iron powder, in sealed gold tubes. Hydrothermal runs were made in conventional cold-seal apparatus. Aenigmatite was synthesized in runs of two to seven days duration at 700 °C (± 5 °C) and 1000 bars $P_{\text{H}_2\text{O}}$. The oxygen fugacity was controlled by the iron-wüstite buffer. Yields of the mineral were above 99 %, indicating that its composition, excepting oxygen, was effectively that of the starting material. Rare high-relief prisms scattered in the aenigmatite powder were tentatively identified as a pyroxene, in negligible quantities.

The aenigmatite formed subhedral prisms, up to 3 μ in length, with an elongation of 3:2 to 3:1. Its pleochroism (pale yellow-brown to very deep red-brown), high

TABLE I. X-ray data for *aemigmatite*

	Kola		Kangerdlussuaq		Synthetic	
	I	d, Å	I	d, Å	I	hkl
vs (1)	8.09	8.09	vs	8.12	vs	001, 010
vw	7.44	7.43	vw	7.47	vw	011
vw	6.36	6.37	vw	6.39	vw	111
w	4.83	4.82	w	4.83	w	011, 111
w	4.41	4.40	w	4.39	w	012, 021
w	4.20	4.20	w	4.20	w	221, 201
vw*	3.79	3.78	vw	3.78	vw	122, 112
mw	3.71	3.70	mw	3.70	mw	022
w	3.490	3.484	w	3.494	w	230, 231, 212
vw*	3.363	3.352	w	3.357	w	111
vw*	3.208	3.237	vw	3.237	vw	130, 102, 121†
vs (2)	3.145	3.150	vs	3.148	vs	012, 021
vw*	3.064	3.046	vw	3.048	vw	122, 321
ms	2.937	2.934	ms	2.937	ms	013, 031, 120
vw*	2.862	2.866	vw	2.864	vw	331, 103
vw	2.806	2.805	vw	2.813	vw	122
vw	2.756	2.752	vw	2.757	w	322, 123, 311
s (3)	2.706	2.700	s	2.706	s	131, 003, 203
vw	2.660	2.656	vw	2.656	vw	113, 300
vw*	2.582	2.584	vw	2.584	—	213, 340
s	2.547	2.544	s	2.544	s	213, 420
vw*	2.513	2.505	vw	2.505	—	141, 322
vw	2.460	2.457	vw	2.457	vw	142, 202
m	2.414	2.412	m	2.413	m	022, 233, 223
vw	2.346	2.347	vw	2.346	vw	140, 440
vw	2.307	2.311	vw	2.311	vw	2.302, 301, 421, 410†
vw*	2.220	2.222	vw	2.222	vw	323, 213, 223†
vw	2.197	2.192	vw	2.192	vw	132, 042, 133
ms	2.119	2.118	ms	2.121	ms	204, 333

	Kola		Kangerdlussuaq		Synthetic	
	I	d, Å	I	d, Å	I	hkl
—	—	—	vw	2.083	vw	252, 350, 352
mw	2.075	—	—	—	—	134, 411
vw*	2.035	2.062	vw	2.062	vw	043, 034, 413†
mw	2.007	2.037	vw	2.037	—	323, 450
vw	1.974	2.010	mw	2.010	mw	122, 250
vw	1.944	1.979	vw	1.979	—	442, 113, 520†
vw	1.907	1.946	vw	1.946	vw	221, 232, 302†
—	—	1.910	vw	1.910	vw	032, 131, 311†
—	—	—	vw	—	vw	1.867
vwB	1.805	1.820	vw	1.820	w B	1.809
vw	1.768	1.797	vw	1.797	—	—
w B	1.732	1.731	w B	1.731	mw B	1.729
w	1.679	1.677	w	1.677	w	1.678
—	—	—	—	—	vw	1.630
m	1.626	1.623	m B	1.623	m	1.620
vw	1.609	1.611	vw	1.611	vw	1.611
vw	1.590	1.589	vw	1.589	vw	1.587
w	1.559	1.560	w	1.560	vw B	1.55
mw	1.513	1.517	mw	1.517	vw	1.514
m	1.497	1.498	m	1.498	vw	1.495
mw	1.483	1.483	mw	1.483	mw	1.480
m B	1.468	1.472	mw	1.472	m B	1.465
w*	1.374	1.374	w	1.374	vw	1.374
w* B	1.348	1.347	w B	1.347	—	—
w* B	1.330	1.334	vw	1.334	vw B	1.336
—	—	1.327	vw	1.327	—	—

* Lines not recorded by Kelsey and McKie (1964). † Plus other possible indices.
Error range allowed in *d*, 2 parts in 1000.

birefringence, and large extinction angle relative to the prism faces were all very similar to those of the naturally occurring mineral. Table I gives X-ray powder data for the synthetic mineral and natural specimens from Kola, U.S.S.R., and Kangerdlugssuaq, East Greenland. Exact localities and chemical analyses for both natural samples, and X-ray powder data for the Kola specimen, are given by Kelsey and McKie (1964).

The powder patterns were obtained using a Philips 11.46-cm diameter camera and Co- $K\alpha$ radiation ($\lambda = 1.79021 \text{ \AA}$), with an Fe filter and Si internal standard. The data for the Kola specimen are in reasonable agreement with those of Kelsey and McKie (1964), except that some additional weak reflections have been observed, of which all with $d > 2.0 \text{ \AA}$ can be indexed successfully. The over-all agreement between the synthetic and natural specimen powder patterns is immediately apparent. However, in detail several minor differences occur; notably at $d = 1.867 \text{ \AA}$, 1.729 \AA , 1.630 \AA , and 1.495 \AA . Nothing can be done to detect the causes of these differences, in the absence of synthetic crystals large enough for single crystal X-ray studies. Kelsey and McKie (1964) have suggested that natural high-temperature (and presumably synthetic) aenigmatite may be monoclinic, because they found specimens from volcanic parageneses to be polysynthetically twinned, whereas the Kola pegmatite specimen studied in detail by them is triclinic and untwinned. The synthetic sample powder pattern is so closely similar to the two natural ones that it seems unlikely that these three specimens belong to differing crystal systems. Thus, synthetic aenigmatite appears to be triclinic, at least at room temperature. The indices of reflections with $d > 2.0 \text{ \AA}$ for all three specimens have been determined on the basis of Kelsey and McKie's (1964) triclinic cell. They correspond to those given by Berry on ASTM card 16-377. A point of interest is that the weak peak on the synthetic specimen pattern at $d = 3.352 \text{ \AA}$ indexes as 111, an index not recorded by Berry.

The pressure ($1 \text{ kb } P_{\text{H}_2\text{O}}$) at which this aenigmatite was synthesized is outside the P - T stability field of Ernst's (1962) titanium-free aenigmatite. This indicates, as would be expected, the larger stability field of the titaniferous phase. A full study of the stability relationships of this aenigmatite is in progress.

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