Kegelite from Tsumeb, Namibia: A redefinition

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Abstract

Kegelite, previously an incompletely described species, is redefined. It is monoclinic, $A2/m$, $A2$, or Am, with $a = 21.04(1)$, $b = 15.55(1)$, $c = 8.986(6)$ Å, and $\beta = 91.0(1)°$. The new chemical formula is $Pb_8Al_4Si_8(SO_4)_2(CO_3)_4(OH)_8O_{20}$, with $Z = 3$.

Introduction

Kegelite was first described from the Tsumeb Mine in Namibia by Medenbach and Schmetzer (1976). The material they studied was not of sufficient quality to permit single-crystal studies, but they were still able to characterize it as a Pb-Zn-Al-sulfosilicate, reporting the formula $Pb_{12}(Zn,Fe)_2Al_4Si_{11}S_4O_{54}$. We have restudied kegelite, using Tsumeb material that has been found to be cospecific with type kegelite; the X-ray powder-diffraction patterns of these two samples are nearly identical. We provide unit-cell data for kegelite and, because our chemical data are at variance with those previously reported by Medenbach and Schmetzer (1976), we propose a new formula on an interim basis. A more precise characterization of the chemical formula of kegelite must await the discovery of material suitable for a crystal structure determination. The sample studied (NMNH no. 147460) is in the collection of the Smithsonian Institution. This redefinition of kegelite was approved by the Commission on New Minerals and Mineral Names, I.M.A.

Description

The sample studied consists of a small, compact mass of pearly white kegelite intimately associated with quartz; some relict galena is also present. The kegelite forms colorless, translucent to transparent, chlorite-like, platy 0.3-mm crystals, with {100} as the dominant form and a perfect {100} cleavage. The crystals are extremely flexible and are distorted by any contact.

The loose, porous nature of the available kegelite aggregates caused determination of the density to be difficult, but it was determined by the position of the densest flakes relative to reference mineral grains distributed in a density gradient in supersaturated Clerici solution (for details see appendix 1). Kegelite was dispersed over a wide density range, apparently owing to varied amounts of adhering and included air bubbles. A small proportion of kegelite flakes was denser than olivenite from the Tintic district, Utah (Mrose obtained a density of 4.46 g/cm³ for material from this area; see Palache et al., 1951). Kegelite flakes were noted down to the level of magnesioferrite from Långban (D = 4.549 − 4.544 g/cm³ for this locality; van de Pijpekamp et al., 1974). This places the density of kegelite at approximately 4.5 g/cm³.

X-ray crystallography

The best kegelite crystals produced rather poor precession photographs and, as a result, crystallographic interpretations were difficult. The extreme flexibility of the crystals resulted in a pronounced streaking of diffraction nodes in all b-axis and c-axis precession photographs. The $0kl$ zone, which produced the best precession photographs, showed only slight deviations of intensity from hexagonal symmetry. Kegelite is monoclinic with the following space-group absence conditions: (a) hkl with $k + l \neq 2n$, (b) $h0l$ with $l \neq 2n$, (c) $0kl$ with $k + l \neq 2n$, and (d) $hk0$ with $k \neq 2n$. The permissible space groups are $A2/m$, $A2$, or Am, and the diffraction aspect is $A*/*$. A fully indexed powder pattern is given in Table 1. Unit-cell parameters, calculated from measurements of zero-level precession films, were refined on the basis of 19 powder reflections. These refined unit-cell parameters are $a = 21.04(1)$, $b = 15.55(1)$, $c = 8.986(6)$ Å, and $\beta = 91.0(1)°$. The cell volume is 2939.5 (5.4) Å³ and the axial ratio $a:b:c = 1.3531:1:0.5779$.

Chemical composition

Kegelite was chemically analyzed using a variety of methods. Heavy elements were determined by electron microprobe, utilizing an operating voltage of 15 kV and a sample current of 0.025 µA, measured on brass. A wavelength-dispersive microprobe scan indicated the absence, in measurable quantities, of any elements with atomic

TABLE 1. X-ray powder data for kegelite

Iest.	dÅ (meas.)	dÅ (calc.)	hkl	Iest.	dÅ (meas.)	dÅ (calc.)	hkl
100	21.0	21.0	100	10	2.531	2.527	$\bar{2}$33*
20	10.5	10.5	200	5	2.412	2.416	$\bar{5}$51
50	7.01	7.01	300*	50	2.339	2.337	900*
30	4.49	4.49	002*	30	2.242	2.246	004*
		4.49	031			2.245	062
20b	4.39	4.41	$\bar{1}$02	15	2.156	2.157	071*
		4.38	102	5	2.133	2.133	362
10	4.09	4.11	202			2.129	304*
80	3.82	3.81	$\bar{3}$02*	5	2.102	2.103	$\bar{1}$000*
40	3.74	3.75	302*			2.088	$\bar{9}$02
15	3.51	3.51	600*	10	2.085	2.084	713
20	3.45	3.45	$\bar{4}$02*			2.084	660*
5	3.053	3.057	531				
		3.045	502				
50	3.006	3.005	700*				
20	2.934	2.941	013*				
		2.940	042				
		2.939	051				
10	2.815	2.817	$\bar{7}$11*				
10	2.747	2.752	631				
		2.741	602*				
5	2.624	2.629	800*				
		2.623	$\bar{6}$22				
90	2.591	2.593	033				
		2.592	060*				

Note: Using a 114.6-mm diameter Gandolfi camera; Fe radiation (λFeKα = 1.9373 Å); intensities estimated visually; b—broad line; indexed on a cell having a = 21.04, b = 15.55, c = 8.986 Å, and β = 91.0°; * = used for unit-cell refinement.

TABLE 2. Chemical analyses of kegelite

	Medenbach and Schmetzer (1976)	Present study
SiO_2	16.3	17.0
Al_2O_3	5.4	7.1
SO_3	7.9	5.5
CO_2	n.g.	7.0
PbO	65.7	60.9
CuO	n.g.	1.5
ZnO	2.8	tr.
FeO	0.95	tr.
CaO	0.04	0.0
MnO	0.01	0.0
H_2O	n.g.	2.6
Total	99.10	101.6

Note: The letters n.g. = not given, tr. = trace.

of the sample used for this analysis showed a weak 3.34 Å reflection attributable to quartz.

The infrared absorption spectrum of the kegelite specimen, which consisted of crystals carefully picked using a binocular microscope for maximum purity, was measured over the 400–4000 cm^{-1} range, using a Perkin-Elmer PE 783 precision grating spectrophotometer. In order to minimize the effects of any moisture absorbed into KBr disks, the spectrum was measured in Nujol mull between KBr plates and also by using a 7-mm pressed-KBr disk containing 0.7 mg of kegelite, with a blank KBr disk containing the same weight of KBr as in the sample disk in the reference beam.

The spectrum conclusively shows the absence of H_2O. (There is no sign of the presence of the H-O-H vibration in the 1600–1650 cm^{-1} region.) The presence of OH in more than one environment is indicated by the OH-stretching vibrations at 3622 and 3400 cm^{-1}. Carbonate shows up strongly, with a very strong absorption at 1390 cm^{-1} and bending vibrations in the 680–860 cm^{-1} region. Stretching vibrations of sulfate and silicate overlap in the 900–1150 cm^{-1} region, with bending vibrations in the 460–610 cm^{-1} region.

The analytical results for kegelite are given in Table 2, together with those of Medenbach and Schmetzer (1976). Our analysis, calculated on the basis of 48 O atoms, gives the empirical formula $Pb_{7.55}Cu_{0.52}Al_{3.85}Si_{7.83}(SO_4)_{1.90}$-$(CO_3)_{4.40}(OH)_{7.98}O_{19.22}$, or, ideally, $Pb_8Al_4Si_8(SO_4)_2(CO_3)_4$-$(OH)_8O_{20}$. With Z = 3 this formula yields a calculated density of 4.76 g/cm^3, which is in good accord with the measured density of approximately 4.5 g/cm^3.

number >9, except those reported in Table 2. The standards employed were synthetic PbO (Pb), celestite (S), synthetic ZnO (Zn), and hornblende (Si, Al, Fe). The data were corrected using a modified version of the MAGIC-4 program. Carbonate was detected by weak effervescence in dilute (1:1) hydrochloric acid and was determined quantitatively using a Leco carbon analyzer. The presence of carbonate in the type material was confirmed.

TGA and EGA (evolved gas analysis) were performed simultaneously on 4 mg of kegelite in vacuum at 10 °C/min, using a Mettler TA-1 THERMOANALYZER/INFICON IQ200 mass spectrometer. There was considerable overlap of H_2O, CO_2, and SO_2 losses, which occurred over the intervals 200–530, 250–700, and 470–930 °C, respectively. Gas pressure maxima for H_2O and CO_2 were noted at 400 (broad peak) and 505 °C, respectively. Two SO_2 pressure maxima were recorded at 770 and 870 °C. There is indirect evidence for Pb volatilization commencing as low as 800 °C. A combined H_2O + CO_2 value of 9.6 ± 0.4 wt% is derived from the loss between 200–615 °C, the relatively large error being due to CO_2-SO_2 overlap. The H_2O and CO_2 contents were estimated from TGA-EGA data as being 2 and 8 wt%, respectively. An H_2O value of 2.6 wt% was obtained by subtracting the 7.0 wt% CO_2 value (obtained by Leco carbon analyzer) from the combined H_2O + CO_2 value of 9.6 wt%. An XRD pattern

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APPENDIX 1: DENSITY DETERMINATION

A 1-ml flat-bottomed glass vial was half filled with Clerici
solution and placed under a heat-lamp in a fume-hood until
steam evolution ceased, which occurred at a temperature where
gas bubbles were just forming. The vial was then cooled and
centrifuged to obtain a metastable density gradient of 4.3 to 4.6
g/cm^3. A sample of kegelite was wetted in saturated Clerici so-
lution and dispersed into small flakes to minimize entrainment
of air bubbles. A few grains of each reference mineral were also
added and wetted. The suspension was then gently placed by
means of a pipette onto the surface of the supersaturated Clerici
solution, and the vial was centrifuged once again. The relative
levels of the various minerals were observed using a stereo mi-
croscope at high magnification, with diffuse illumination through
the bottom of the vial.