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Properties of synthetic Cs-dioctahedral hydrous mica, $CsGa_2(Ga, Ge_3)O_{10}(OH)_2$

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Abstract

A Cs-dioctahedral gallogermanate mica, $CsGa_2(Ga,Ge_3)O_{10}(OH)_2$, was synthesized under hydrothermal conditions: 300°C, 100 kg/cm^2, and 23 days. The cell parameters of this mica are of the 1M type, with $a = 5.412(1)$, $b = 9.366(3)$, $c = 11.427(2)$A, $\beta = 101.22(2)°$, with standard deviations in parentheses. The infrared spectrum of this Cs-mica is very similar to those of other gallogermanate K^+ and Rb^+ micas. In the far infrared absorption spectrum, out-of-plane and in-plane stretching vibrations of Cs–O are recognized below 100 cm^{-1}.

Introduction

In the course of systematic synthesis of hydrous dioctahedral micas substituted by several cations, a Cs-mica, $CsGa_2(Ga,Ge_3)O_{10}(OH)_2$ was synthesized. There has been, to my knowledge, no report on the complete substitution of cesium in the interlayer position of hydrous dioctahedral micas. The present study gives experimental results on the properties of this mica, which possesses two kinds of gallium cations that are four- and six-coordinated by oxygen.

Experimental

The mica was synthesized from reagent grade $Cs_2CO_3:Ga_2O_3:GeO_2 = 1:1:2$. Each of these mixtures was sealed in a silver capsule with excess distilled water, homogenized by an ultrasonic washer for fifteen minutes, and reacted in the Morey-type autoclave at 300°C, 100 kg/cm^2, for 23 days. The resulting white powder was washed with distilled water, dried at 110°C, and then analyzed.

X-ray analysis

X-ray powder analysis was made with a RIGAKU Geigerflex diffractometer using Cu*Kα* radiation with silicon internal standard. X-ray powder data for synthetic Cs-mica are given in Figure 1 and Table 1. Cell parameters, determined by refinement of X-ray diffractometer data with the modified RSLC-3 of UNICS computer program (Sakurai, 1967) are displayed in Table 2 with those of other gallogermanate micas, $RbGa_2(Ga,Ge_3)O_{10}(OH)_2$, $KGa_2(Ga,Ge_3)O_{10}(OH)_2$ (Kimata, 1979), and $NH_4Ga_2(Ga,Ge_3)O_{10}(OH)_2$ (Barrer and Dicks, 1966). The polytype of this Cs-mica is 1M, based on the appearance of 112 and $\bar{1}12$ reflections (Smith and Yoder, 1956). The difference in cell parameters between these micas results from the difference in ionic radii between Cs^+ (1.70A), Rb^+ (1.49A), and K^+ (1.38A) (Shannon and Prewitt, 1969) and NH_4^+ (1.43A; Goldschmidt, 1954, p. 89), as is shown for *d*(001) in Figure 2. The same linear relation is reported for dioctahedral hydrous silicate micas (Eugster and Munoz, 1966). Although NH_4 is a nonspherical cation (it is tetrahedral), Figure 2 casts doubt on the accuracy of either the assumed ionic radius of NH_4^+ cation or the cell parameters of NH_4-mica.

Scanning electron microscopic analysis

The mica was examined with a HITACHI scanning electron microscope, S-450. As shown in Figure 3, this Cs-mica grows as thin, well-formed plates, approximately hexagonal in outline. It has a pearly lustre and is colorless under the polarization microscope. The above characters are common to dioctahedral aluminosilicate micas.

Infrared absorption analysis

A spectrophotometer tracing illustrating the infrared absorption is shown in Figure 4. The KBr disk method was used, and measurements were made with a Japan Spectroscopic IR-G double beam spectrophotometer, using a polystyrene standard. The infrared spectra of K–, Rb– and Cs-gallogermanate micas in the range 4000 to 400 cm^{-1} are very similar. Thus OH vibrations appear to be little affected by interlayer cations.

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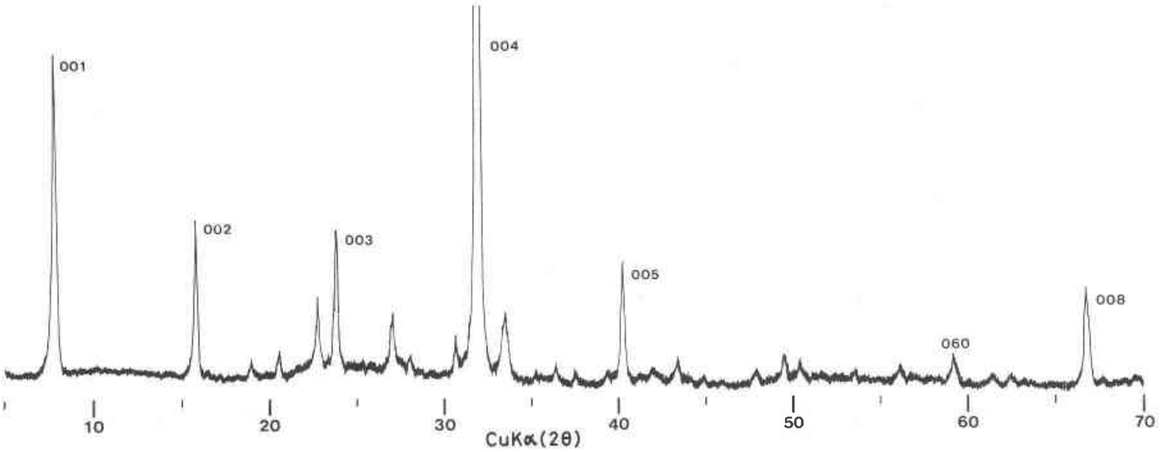

Fig. 1. X-ray powder pattern of synthetic Cs-mica.

The most noticeable difference between the infrared spectra of orthogermanates (Tarte, 1962, 1963a, b) and the layer germanates (Kimato, 1979) is the shift of bands due to Ge–O stretching vibrations towards low frequencies. The main Ge–O stretching vibration is observed at about 800 cm^{-1} in germanate micas, whereas it is at about 700 cm^{-1} in orthogermanates. This shift may be due to structural changes in the linking mode of the GeO_4 tetrahedra. The characteristic frequency range, which is 800–700 cm^{-1} for GeO_4 tetrahedra in orthogermanates, falls to 650 cm^{-1} or below for GeO_6 octahedra (Tarte and Ringwood, 1964). This drop in frequency caused by change of coordination number is expected to be visible in the Ga–O vibrational range. This Cs-mica has four Ga atoms in the octahedra of its unit cell and two Ga atoms in the tetrahedra, from which it is reasonable to conclude that the stretching vibration of Ga^{VI}–O is stronger in absorption percent than that of Ga^{IV}–O. Accordingly the band at 925 cm^{-1} may be assigned to the Ga^{IV}–O stretching vibration, while that at 833 cm^{-1} to that of Ga^{VI}–O. Farmer (1972, p. 8) summarized the effect of coordination, especially tetrahedral and octahedral coordination, on stretching frequencies. Such a difference in wavenumber between Ga^{IV}–O and Ga^{VI}–O stretching vibrations

Table 1. X-ray powder data for $CsGa_2(Ga,Ge_3)O_{10}(OH)_2$

hkl	$d_{obs.}$(Å)	$d_{calc.}$(Å)	I
001	11.24	11.208	22
002	5.608	5.604	11
020	4.671	4.683	2
021	4.318	4.321	2
$\bar{1}12$	3.909	3.903	2
003	3.735	3.736	10
022	3.594	3.593	4
112	3.303	3.300	5
$\bar{1}13$	3.182	3.180	2
023	2.915	2.920	3
004	2.803	2.802	100
$\bar{1}31$	2.679	2.677	5
$\bar{1}32$	2.524	2.525	1
201	2.469	2.477	2
$\bar{2}03$	2.397	2.395	1
041	2.290	2.292	1
005	2.241	2.241	8
221	2.190	2.189	1
133	2.088	2.088	2
222	2.019	2.018	1
134	1.8529	1.8519	1
$\bar{1}16$	1.8437	1.8438	2
$\bar{1}35$	1.8112	1.8127	2
$\bar{1}53$	1.6385	1.6386	2
$\bar{3}31$ 060	1.5607	1.5614 1.5611	2
225	1.4874	1.4876	1
136	1.4689	1.4683	1
008	1.4003	1.4011	7
$\bar{3}35$	1.3832	1.3831	1
$\bar{2}08$	1.3526	1.3526	1

Table 2. Crystallographic data for gallogermanate micas (standard errors in parentheses)

	This study	Kimata (1979)		Barrer and Dicks (1966)
	Cs-mica	Rb-mica	K-mica	NH_4-mica
a (Å)	5.412(1)	5.430(3)	5.377(3)	5.42
b (Å)	9.366(3)	9.346(3)	9.317(4)	9.33
c (Å)	11.427(2)	21.957(9)	20.917(7)	21.957
β (°)	101.22 (2)	101.66 (8)	95.36(11)	101.4
V (Å^3)	568.2 (3)	1091.5(8)	1043.4(9)	1088.4
ρ (g/cm^3)*	4.408	4.300	4.203	3.901
Polytype	1M	2M	2M	2M

Cs-mica; $CsGa_2(Ga,Ge_3)O_{10}(OH)_2$,
Rb-mica; $RbGa_2(Ga,Ge_3)O_{10}(OH)_2$,
K-mica; $KGa_2(Ga,Ge_3)O_{10}(OH)_2$,
NH_4-mica; $NH_4Ga_2(Ga,Ge_3)O_{10}(OH)_2$.
* the calculated density.

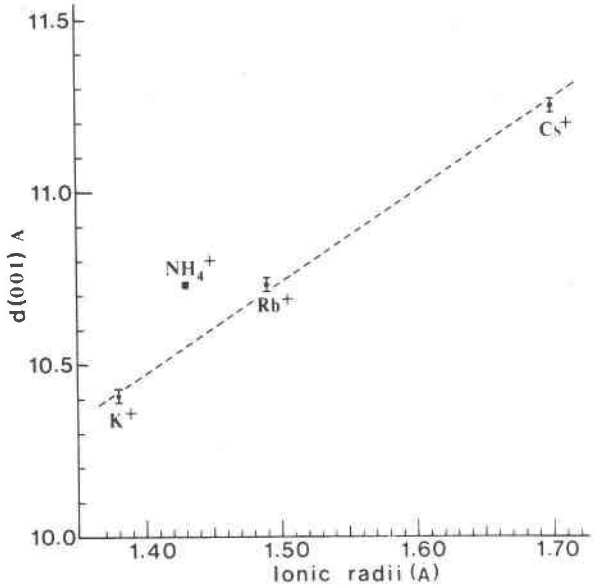

Fig. 2. Spacing of (001) for assumed 1M polymorphs of synthetic dioctahedral micas as a function of the ionic radius of the interlayer cation.

seems probable by reference to the effect of coordination number on stretching vibrations of Al–O and Fe^{3+}–O as reported by Farmer. The splitting of the absorption band at approximately 900 cm^{-1} implies the deformation of the tetrahedral sites of Ga cations.

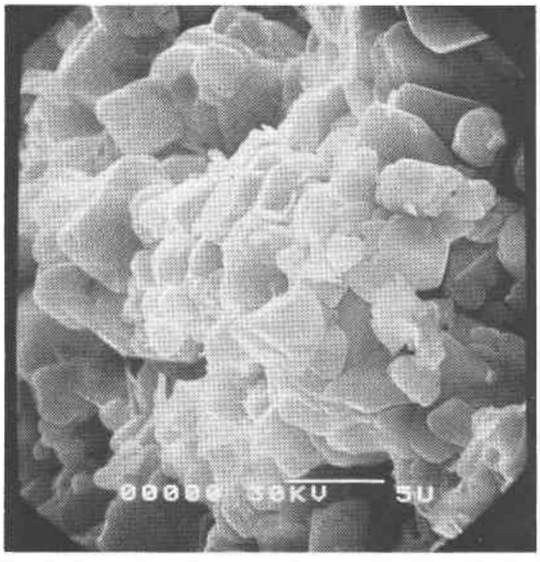

Fig. 3. Scanning electron micrograph of synthetic Cs-dioctahedral mica. Bar is 5 microns.

Far infrared absorption analysis

The far infrared (FIR) study was made by the polystyrene plate method, in which a small amount of specimen powder was placed between two films. The measurements were made with a HITACHI FIS-070 vacuum spectrophotometer in the frequency range from 50 to 400 cm^{-1}. The resulting curve is represented in Figure 5. The vibrations of the interlayer cations occur from 50 to 200 cm^{-1}.

In the FIR spectrum of pollucite, $CsAlSi_2O_6 \cdot H_2O$ (Kimata, unpublished data), there is a very strong absorption band near 100 cm^{-1}. This band is assigned to Cs–O stretching vibration, and so the stronger band at 95 cm^{-1} of this synthetic Cs-mica may also be assigned to Cs–O stretching. Kimata (1979) assigned the out-of-plane and in-plane vibrations of Rb–O and K–O in hydrous dioctahedral gallogermanate micas. Their relationship is shown in Figure 6, with the FIR data for Cs-mica. This figure suggests that out-of-plane and in-plane vibrations of Cs–O in this mica are at 95 and 65 cm^{-1} respectively. This assignment is based on the assumption that if the ion is similar in its charge, the bands related to the larger ionic radius and larger ionic mass are in a lower frequency region than the bands related to the smaller ionic radius and smaller ionic mass.

Differential thermal analysis

The DTA and TG curves of these micas were measured in air with a RIGAKU thermoflex under the following conditions: thermoflex Pt–PtRh; reference, Al_2O_3; mean heating rate, 10°C/min; sensitivity(DTA), ±250 μV; sensitivity(TG), 5 mg; sample weight, about 17 mg; temperature range 15–1000°C. This Cs-mica has one broad endothermic peak at 545°C accompanied by a weight loss, which is interpreted to be due to loss of octahedral OH. The dehydration temperature of synthetic Cs-mica is slightly lower than those of Rb- and K-gallogermanate hydrous micas (Kimata, 1979). Since IR data suggest that the OH-bonding state in these micas is very similar, this difference in dehydroxylation temperature may be due to the particle size of synthesized crystals.

Conclusion

The properties of hydrous Cs-dioctahedral gallogermanate micas are very similar to those of hydrous Rb-dioctahedral gallogermanate micas. The IR data for these Cs-, Rb-, and K-micas show that the bonding state of the OH anion in these micas makes little difference.

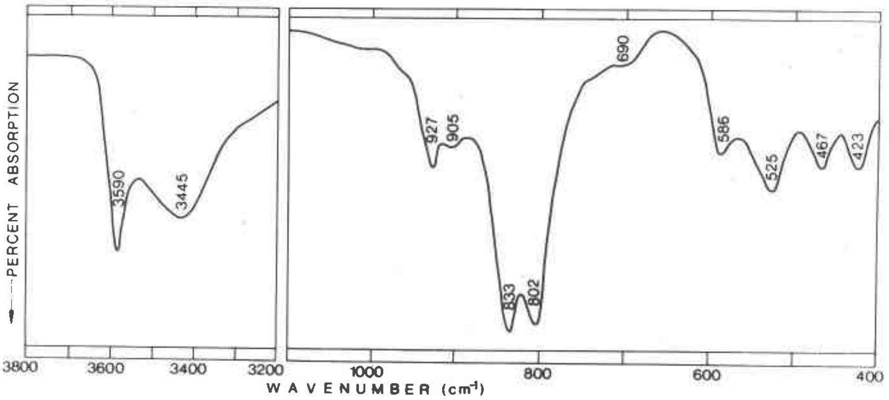

Fig. 4. The infrared absorption spectrum of synthetic Cs-mica.

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References

Barrer, R. M. and L. W. Dicks (1966) Chemistry of soil minerals. Part III. Synthetic micas with substitutions of NH_4 for K, Ga for Al, and Ge for Si. *J. Chem. Soc., (A),* 1379–1385.

Eugster, H. P. and J. Munoz (1966) Ammonium micas: possible sources of atmospheric ammonia and nitrogen. *Science, 151,* 683–686.

Farmer, V. C. (1972) *The Infrared Spectra of Minerals.* Mineralogical Society, London.

Goldschmidt, V. M. (1954) *Geochemistry.* Clarendon Press, Oxford.

Kimata, M. (1979) Synthesis and properties of a Rb-dioctahedral mica, $RbGa_2(Ga,Ge_3)O_{10}(OH)_2$. *Neues Jahrb. Mineral. Monatsh.,* in press.

Sakurai, T. (1967) *RSLC-3, Universal Crystallographic Computation Program System (II) (UNICS).* The Crystallographic Society, Japan.

Shannon, R. D. and C. T. Prewitt (1969) Effective ionic radii in oxides and fluorides. *Acta Crystallogr., B25,* 925–946.

Smith, J. V. and H. S. Yoder (1956) Experimental and theoretical studies of the mica polymorphs. *Mineral. Mag., 31,* 209–235.

Tarte, P. (1962) Infrared study of orthosilicates and orthogermanates. New method for interpretation of spectra. *Spectrochim. Acta, 18,* 467–483.

——— (1963a) Infrared study of orthosilicates and orthogermanates. II. Olivine and monticellite structures. *Spectrochim. Acta, 19,* 25–47.

——— (1963b) Infrared study of orthosilicates and orthogermanates. III. Spinel structures. *Spectrochim. Acta, 19,* 49–71.

——— and A. E. Ringwood (1964) Infrared spectrum and germanium coordination in some high-pressure metagermanates. *Nature, 201,* 819.

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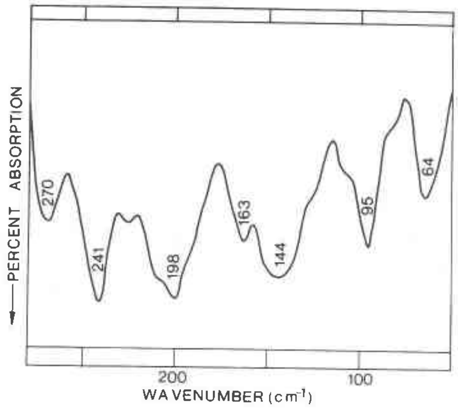

Fig. 5. The far infrared absorption spectrum of synthetic Cs-mica.

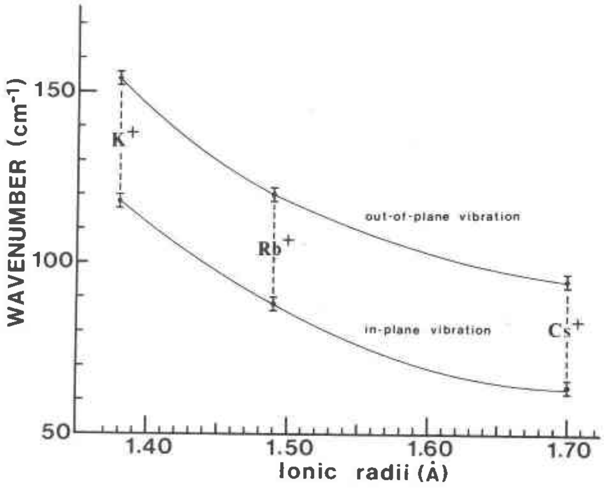

Fig. 6. The relation between stretching vibrations of alkali cation–oxygen and the ionic radius of the interlayer alkali cation.