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STRUCTURAL CHEMISTRY OF BARYSILITE-TYPE COMPOUNDS $XY_2(Pb_2Si_2O_7)_3$

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ABSTRACT

There is a negative linear correlation ($\hat{R} = -0.96$) between the axial ratio c/a and the radii of divalent metal cations occupying the X site in barysilite-type compounds. The substitution of larger atoms leads to a broadening of the characteristic channels in the $(Pb_2Si_2O_7)^{2-}$ framework.

INTRODUCTION

Compounds isotypic with barysilite, $MnPb_8(Si_2O_7)_3$, have been synthesized by Lajzerowicz (1966), Ito and Frondel (1967), Billhardt (1969), Bordeaux and Lajzerowicz (1969), and others (for a survey see Billhardt, 1969). In these compounds Mn has been replaced by Mg, Ca, Sr, Ba, Fe, Co, Ni, Cu, Zn, Cd, and Pb. The space group is $R\bar{3}c$, the hexagonal lattice constants are $a \sim 10$ Å, $c \sim 38$ Å, and the density is ~6.8 g/cc.

The crystal structures of only two barysilites have been determined: $MnPb_8(Si_2O_7)_3$ by Lajzerowicz (1966) and its lead analogue, $Pb_3Si_2O_7$, by Petter *et al.* (1971). The barysilite structure is built up of a $(Pb_2Si_2O_7)^{2-}$ framework characterized by distinct channels parallel to c (Petter and Harnik, 1971). The framework consists of (001) "sheets" of symmetrically equivalent Si_2O_7 double tetrahedra which are linked three-dimensionally by Pb atoms. The remaining metal atoms lie inside the channels in Y-X-Y chains with distances of approximately 3.5 Å between the atoms in the chain and 12 Å between adjacent chains. According to the chemical analyses published, exchanges of metal atoms have been observed *only at the* X *site.*

In the present work the lattice parameters of barysilite compounds have been calculated and are compared, and their dependence on various divalent metal cations (Mg, Ca, Sr, Ba, Mn, Fe, Co, Ni, Cu, Zn, Cd, and Pb) occupying the six-coordinated X site is discussed. Table 1 gives the lattice parameters and axial ratios of sixteen samples representing twelve different barysilite compounds. Most parameters have been obtained by least-squares refinement of published, but not previously indexed, powder diagrams. Data from two additional samples are included in the table, but no use has been made of them because

Table 1. Lattice Parameters and Axial Ratio

Composition	a_h [Å]	c_h [Å]	Parameters from: + own calculation o literature, based on () reflexions	c/a	Locality (S = synthetic)	Referenc
$PbPb_2(Pb_2Si_2O_7)_3$	10.1264(3)[a]	38.678(2)[a]	o (84)	3.8195(2)[a]	S	b
$PbPb_2(Pb_2Si_2O_7)_3$	10.130(6)	38.70(3)	o	3.820(4)	S	d
$PbPb_2(Pb_2Si_2O_7)_3$	10.204(4)	38.977(20)	o	3.820(3)	S	f
$MnPb_2(Pb_2Si_2O_7)_3$	9.821(5)	38.38(6)	o	3.908(6)	Långban, Sweden	c
$MnPb_2(Pb_2Si_2O_7)_3$	9.80(1)	38.35(5)	o	3.913(7)	Långban, Sweden	d
$SrPb_2(Pb_2Si_2O_7)_3$	10.091(6)	38.72(3)	o	3.837(4)	S	d
$BaPb_2(Pb_2Si_2O_7)_3$	10.166	38.91	o	3.83	S	d
$MgPb_2(Pb_2Si_2O_7)_3$	9.75(3)	38.28(6)	o	3.926(14)	S	d
$MgPb_2(Pb_2Si_2O_7)_3$	9.78(1)	38.36(8)	+ (6)	3.922(9)	S	e
$NiPb_2(Pb_2Si_2O_7)_3$	9.749(5)	38.28(4)	+ (6)	3.927(5)	S	e
$CoPb_2(Pb_2Si_2O_7)_3$	9.779(6)	38.32(4)	+ (6)	3.919(5)	S	e
$CuPb_2(Pb_2Si_2O_7)_3$	9.79(1)	38.22(8)	+ (6)	3.904(9)	S	e
$FePb_2(Pb_2Si_2O_7)_3$	9.787(9)	38.35(7)	+ (6)	3.919(8)	S	e
$ZnPb_2(Pb_2Si_2O_7)_3$	9.805(7)	38.38(5)	+ (6)	3.914(6)	S	e
$CdPb_2(Pb_2Si_2O_7)_3$	9.884(6)	38.50(4)	+ (6)	3.895(5)	S	e
$CaPb_2(Pb_2Si_2O_7)_3$	9.92(2)	38.4(2)	+ (6)	3.87(2)	S	e
$((Mn,etc.)Pb_4Si_3O_{11})_3$[i]	9.80(1)	38.3(1)	+ (6)	3.91(1)	Franklin, N.J. U.S.N.M. C-6389	g
$MgPb_8(Si_2O_7)_3$[h,i]	9.73(5)	38.24(10)	o	3.93(2)	S	d

[a] Estimated standard errors in brackets refer to the last decimal digit.

[b] Petter, Harnik and Keppler (1971).

[c] Lajzerowicz (1966).

[d] Billhardt (1969).

[e] Ito and Frondel (1967).

[f] Bordeaux and Lajzerowicz (1969).

[g] Glasser (1964).

[h] Originally, Argyle and Hummel (1965/66) characterized this compound as $Pb_2MgSi_2O_7$.

[i] These data are not used in Figure 1.

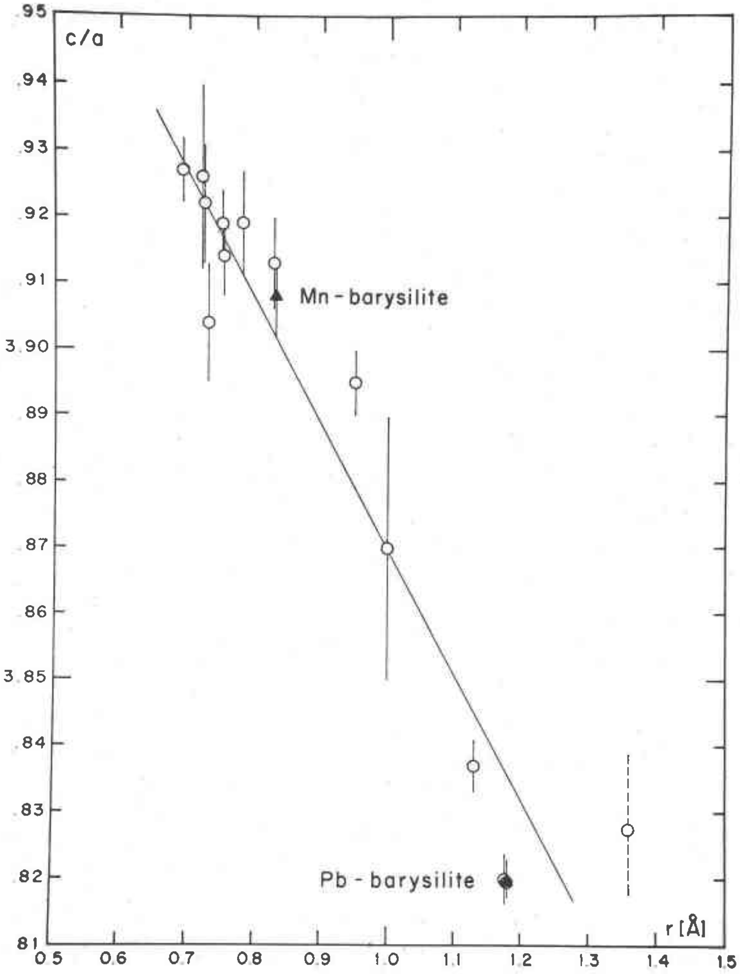

FIG. 1. Plot of the axial ratio c/a versus the divalent ionic radius r (Shannon and Prewitt, 1969) for six-coordinated metal cations at the X site. The correlation coefficient $\hat{R} = -0.96$. Triangles indicate compounds whose structures have been determined, circles other data from Table 1. The vertical bars are estimated standard errors, except for the lower right data point whose errors were not reported.

they have not been established without doubt as belonging to the barysilite group.

AXIAL RATIO c/a AND IONIC RADIUS

To see if not only the size of the unit cell but also the shape of the $(Pb_2Si_2O_7)^{2-}$ framework is being changed by putting cations of different

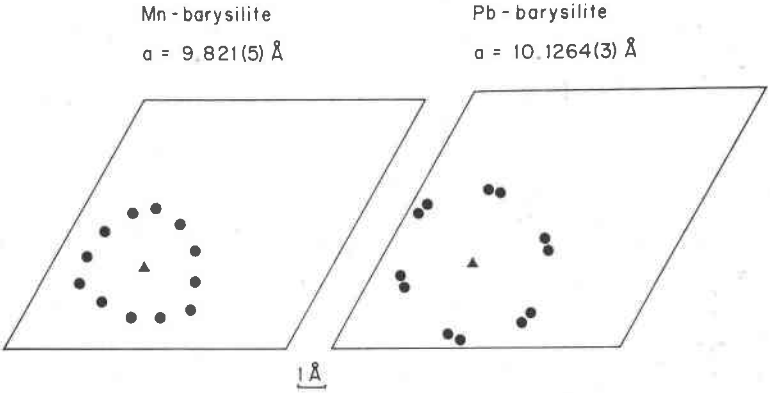

FIG. 2. Schematic representation of channel cross-sections comparing Mn-barysilite (Lajzerowicz, 1966) and Pb-barysilite (Petter *et al.*, 1971) in a (001) projection. Only the centers of the oxygen atoms forming one channel are shown. The position of the X atoms is on the 3 axis.

radius into the X site, the axial ratio c/a has been plotted versus the radius r. Figure 1 shows a negative linear correlation ($\hat{R} = -0.96$) between the axial ratio and the cation radius. It is obvious that the shape of the framework changes with substitution of increasingly larger cations at the X site.

The nature of that change can be visualized in schematic (001) channel cross-sections of Mn- and Pb-barysilites (Figure 2). The mean channel diameter in Pb-barysilite is considerably larger and the cross-section more nearly circular than the one in Mn-barysilite. The broadening of the channels means that with increasing r the framework tends to expand primarily along the a axis.

The coordination of oxygen around the central chain atom X was reported to be a slightly flattened octahedron in Mn-barysilite and, in Pb-barysilite, a trigonal "antiprism", the top face of which is rotated out of the prism position by 23.2° relative to the bottom face. Therefore the investigation of possible correlations between ionic radii and polyhedra size and shape will be one of the aims of future structure determinations of barysilite-type compounds in this laboratory.

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REFERENCES

ARGYLE, J. F., AND F. A. HUMMEL (1965/66) The system PbO-BaO-MgO-SiO$_2$. Phase studies in subsidiary ternary systems. *Glass Ind.* **46**, 583–587, 627–628, and 710–718; **47**, 20–25.

BILLHARDT, H. W. (1969) Synthesis of lead pyrosilicate and other barysilite-like compounds. *Amer. Mineral.* **54**, 510–521.

BORDEAUX, D., AND J. LAJZEROWICZ (1969) Synthèse de la barysilite $Pb_3Si_2O_7$. *Bull. Soc. Franc. Mineral. Cristallogr.* **92**, 383–385.

GLASSER, F. P. (1964) New data on barysilite. *Amer. Mineral.* **49**, 1485–1488.

ITO, J., AND C. FRONDEL (1967) Syntheses of lead silicates: Larsenite, barysilite and related phases. *Amer. Mineral.* **52**, 1077–1084.

LAJZEROWICZ, J. (1966) Etude par diffraction des rayons X et absorption infrarouge de la barysilite, $MnPb_8 \cdot 3Si_2O_7$, et de composés isomorphes. *Acta Crystallogr.* **20**, 357–363.

PETTER, W., AND A. B. HARNIK (1971) Der Strukturtyp des Barysilit, $XY_2(Pb_2Si_2O_7)_3$. *Fortschr. Mineral.* **49**, 39–40.

PETTER, W., A. B. HARNIK, AND U. KEPPLER (1971) Die Kristallstruktur von Blei-Barysilit, $Pb_3Si_2O_7$. *Z. Kristallogr.* **133**, 445–458.

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

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SAMPLE PREPARATION FOR X-RAY FLUORESCENCE ANALYSIS: LI-BORATE GLASS DISKS

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INTRODUCTION

X-ray fluorescence analysis is a widely accepted technique for obtaining rapid chemical analyses of geologic samples. Problems have arisen, however, in sample preparation that is fast, reproducible and inexpensive, and which produces a durable, long-lived standard or sample.

Claisse (1956) pioneerd the flux-fusion technique for preparation of X-ray fluorescence samples. Subsequent modifications by Rose, Adler, and Flanagan (1962) have been widely adopted. However, fluorescence samples prepared by briquetting crushed glass boules are susceptible to contamination, are subject to deterioration, and require finely-machined dies and a laboratory press. A fused glass disk sample preparation has been described by Norrish and Hutton (1968), but the writers experienced difficulty preparing disks that did not crack upon removal from the graphite mold. The writers' proposed technique is similar to that developed by Stephenson (1969), but eliminates the oven annealing process designed to relieve stress within