

Determination of Ternary-System Cation Distribution in (Co,Ni,Zn)SiO₃ Pyroxene Employing Two-Wavelength Anomalous Dispersion with Synchrotron Radiation

BY KATSUHIRO TSUKIMURA

Geological Survey of Japan, Higashi, Tsukuba 305, Japan

SATOSHI SASAKI

Photon Factory, National Laboratory for High Energy Physics, Oho, Tsukuba 305, Japan

AND HARUO OHASHI

National Institute for Research in Inorganic Materials, Namiki, Tsukuba 305, Japan

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Abstract

(Co_{1/3},Ni_{1/3},Zn_{1/3})SiO₃, $M_r = 137.088$, orthorhombic, *Pbca*, $a = 18.209$ (1), $b = 8.915$ (1) and $c = 5.2182$ (4) Å, $V = 847.1$ (1) Å³, $Z = 16$, $D_x = 4.300$ g cm⁻³, $T = 300$ K. Lattice, positional and thermal parameters were determined with Mo $K\alpha$ radiation; $F(000) = 1061$ and $R = 0.036$ for 2514 symmetry-independent reflections with $F > 3\sigma(F)$. The metal atoms, Co, Ni and Zn, are distributed statistically between $M1$ and $M2$ sites. This ternary-system cation distribution was determined from two sets of intensity data collected using synchrotron radiation at two different wavelengths (1.6168 and 1.4948 Å), which are 0.01 Å longer than the Co and Ni K absorption edges, respectively. These wavelengths were selected because the anomalous-dispersion effects of Co and Ni are large. The R value was 0.029 for Co K edge data and 0.033 for Ni K edge data. Both data sets include 157 symmetry-independent reflections with $F > 3\sigma(F)$. The occupancies are 0.273Co + 0.530Ni + 0.197Zn in the $M1$ sites and 0.394Co + 0.137Ni + 0.469Zn in the $M2$ sites.

1. Introduction

Synchrotron radiation has accelerated the study of intersite cation distribution, especially in crystals having cations close in atomic number. The real part of the anomalous-dispersion factor for an atom is negatively large when the X-ray wavelength is close to the absorption edge. If we use the X-ray wavelength close to the lighter atom's absorption edge, the difference of the scattering factors between the two cations becomes large. This anomalous-dispersion method has been applied to the determination of the cation distributions of (Co,Fe)₃O₄ (Yakel, 1980), Cr₄₈Fe₅₂ (Yakel, 1983) and (Fe,Ni)₉S₈ (Tsukimura, 1989). This method has, however, been

restricted so far to determining the distribution of two kinds of cations.

The present study has determined the ternary-system cation distribution in (Co,Ni,Zn)SiO₃ pyroxene using two sets of intensity data and employing the anomalous-dispersion effect. The anomalous-dispersion method using one set of intensity data cannot determine a ternary-system cation distribution, but this becomes possible if we use two sets of intensity data measured at two different wavelengths.

The (Co_{1/3},Ni_{1/3},Zn_{1/3})SiO₃ pyroxene has an orthopyroxene structure, which has two metal sites, $M1$ and $M2$, in the SiO₃ chains. The Co, Ni and Zn atoms are statistically distributed between the $M1$ and $M2$ sites. Cation distributions of orthopyroxenes have been determined for (Mg,Mn)SiO₃, (Mg,Fe)-SiO₃, (Mg,Ni)SiO₃, (Mg,Co)SiO₃ and (Mg,Zn)SiO₃ by Ghose, Wan & Okamura (1975), and for (Mg,Zn)SiO₃ by Morimoto, Nakajima, Syono, Akimoto & Matsui (1975). These are binary-system pyroxenes and the atomic numbers of the two cations are considerably different, so that the distributions could be determined by conventional X-ray diffraction techniques.

2. Two-wavelength anomalous-dispersion method

This section shows that the determination of a ternary-system cation distribution with cations close in atomic number needs two sets of intensity data collected at two different wavelengths. The scattering factors of the Co, Ni and Zn atoms are approximated as

$$\begin{aligned} f_{\text{Co}}(\sin\theta/\lambda, \lambda) &= a_{\text{Co}}(\lambda)f_0(\sin\theta/\lambda) \\ f_{\text{Ni}}(\sin\theta/\lambda, \lambda) &= a_{\text{Ni}}(\lambda)f_0(\sin\theta/\lambda) \\ f_{\text{Zn}}(\sin\theta/\lambda, \lambda) &= a_{\text{Zn}}(\lambda)f_0(\sin\theta/\lambda) \end{aligned} \quad (1)$$

where f_0 is normalized so that $f_0(0) = 1$. When the anomalous-dispersion effect is neglected, a_{Co} , a_{Ni} and a_{Zn} are atomic numbers. The scattering factor of the $M1$ sites is

$$f_{M1}(\sin\theta/\lambda, \lambda) = X_{\text{Co}} f_{\text{Co}}(\sin\theta/\lambda, \lambda) + X_{\text{Ni}} f_{\text{Ni}}(\sin\theta/\lambda, \lambda) + X_{\text{Zn}} f_{\text{Zn}}(\sin\theta/\lambda, \lambda) \\ = f_0(\sin\theta/\lambda) [a_{\text{Co}}(\lambda) X_{\text{Co}} + a_{\text{Ni}}(\lambda) X_{\text{Ni}} + a_{\text{Zn}}(\lambda) X_{\text{Zn}}] \quad (2)$$

where X_A is the mole fraction of A atoms in the $M1$ sites. Diffraction experiments give the value of f_{M1}/f_0 [$\equiv b(\lambda)$]. Then we have the equation:

$$a_{\text{Co}}(\lambda) X_{\text{Co}} + a_{\text{Ni}}(\lambda) X_{\text{Ni}} + a_{\text{Zn}}(\lambda) X_{\text{Zn}} = b(\lambda). \quad (3)$$

The total occupancy of the $M1$ sites is assumed as

$$X_{\text{Co}} + X_{\text{Ni}} + X_{\text{Zn}} = 1. \quad (4)$$

We have three unknown parameters X_{Co} , X_{Ni} and X_{Zn} in two equations (3) and (4).

Intensity measurements at a different wavelength employing the anomalous-dispersion effect of a cation can give further data:

$$a_{\text{Co}}(\lambda') X_{\text{Co}} + a_{\text{Ni}}(\lambda') X_{\text{Ni}} + a_{\text{Zn}}(\lambda') X_{\text{Zn}} = b(\lambda'). \quad (5)$$

Then we have three independent equations, (3), (4) and (5) and three unknown parameters. Thus, we can obtain the most probable occupancy in the ternary system.

3. Experimental

3.1. Samples

Single crystals of (Co_{1/3},Ni_{1/3},Zn_{1/3})SiO₃ orthopyroxene were synthesized at 1573 K and 6 GPa for 20 h in a Pt capsule, using the Belt-type high-pressure apparatus with a graphite heater. The crystal examined in this study was ground into a sphere 0.13 mm in diameter. The damaged surface resulting from grinding was chemically etched away.

3.2. Mo $K\alpha$ data

Intensity data were collected with conventional Mo $K\alpha$ radiation ($\lambda = 0.7107 \text{ \AA}$) at room temperature in either the ω scan mode ($2\theta < 40^\circ$) or the ω - 2θ scan mode ($40 \leq 2\theta < 130^\circ$) using a Rigaku AFC-5 four-circle diffractometer. The reflection data within the blind area of the bisecting setting were collected with the $\chi - 90^\circ$ setting. Each reflection was scanned at 2° min^{-1} in ω with a scan width of $(1.2 + 0.35 \tan\theta)^\circ$. Intensity measurements were repeated up to three times for each reflection; the criterion was $\sigma(F)/F$ smaller than 0.2. A standard reflection was stable within 0.5% of the integrated intensity during data collection. A set of intensities were corrected for Lorentz and polarization factors.

Table 1. *Orthopyroxene* (Co,Ni,Zn)SiO₃: crystal and experimental data

	Co K edge	Ni K edge	Mo $K\alpha$
Wavelength (\AA)	1.6168	1.4968	0.7107
Linear absorption coefficient (cm^{-1})	185	311	100
Transmission factors			
Minimum	0.19	0.07	0.39
Maximum	0.22	0.11	0.44
Maximum 2θ ($^\circ$)	80	73	130
No. of reflections			
Measured	208	205	4653
Used for refinements	157	157	2514
R factor	0.029	0.033	0.036
wR factor	0.032	0.032	0.032

Lattice parameters were determined from 16 reflections ($86 < 2\theta < 93^\circ$). The experimental data are summarized in Table 1.

3.3. Synchrotron radiation data

The synchrotron radiation measurements were carried out at the Photon Factory, National Laboratory for High Energy Physics, Japan. X-rays from a normal-bending magnet were used with a tunable Si(111) monochromator on a vertical-type four-circle diffractometer at the BL-10A station. Complete intensity profile data for each Bragg reflection in $1/8$ of reciprocal space for $\sin\theta/\lambda = 0.04 \text{ \AA}^{-1}$ were collected with the ω - 2θ step-scan mode. Each profile has 75 steps at intervals of 0.02° in ω . Each step was measured for 1 s. The wavelengths used, 1.6168 \AA (7.668 keV) and 1.4968 \AA (8.283 keV), were 0.01 \AA longer than those of Co and Ni K absorption edges, respectively. We found the absorption edges by scanning the wavelength and measuring the intensity of the monochromated incident beam transmitted through Co or Ni metal foils, then shifting the wavelength by 0.01 \AA to the longer side of the absorption edge. The storage ring was operated at 2.5 GeV and 150–80 mA and was stable throughout the experiment (about 8 h). The decrease of the intensity of the X-ray beam was monitored with a standard reflection measured every ten reflections and could be easily corrected using the intensity of the standard reflection. Integrated intensities were corrected for the Lorentz factor. The polarization factor was assumed to be unity because the electric vector of the incident beam was about 100% polarized in a direction perpendicular to the scattering plane.

3.4. Crystal structure refinements

We used atomic scattering factors in the form of $f = f_o + f' + if''$, where f_o is the Thomson scattering factor and f' and f'' are anomalous-scattering factors. The Thomson scattering factors are taken from *International Tables for X-ray Crystallography*

Table 2. *Orthopyroxene* (Co,Ni,Zn)SiO₃: *anomalous-dispersion factors*

The values are taken from Sasaki (1984).

Wavelength (Å)		Co K edge 1.6168	Ni K edge 1.4968	Mo K α 0.7107
Co	f'	-4.976	-1.845	0.299
	f''	0.478	3.453	0.973
Ni	f'	-2.276	-4.820	0.289
	f''	0.555	0.483	1.113
Zn	f'	-1.434	-1.752	0.222
	f''	0.739	0.643	1.431
Si	f'	0.256	0.233	0.072
	f''	0.360	0.313	0.071
O	f'	0.050	0.043	0.008
	f''	0.036	0.030	0.006

Table 3. *Orthopyroxene* (Co,Ni,Zn)SiO₃: *positional and isotropic temperature factors*

	x	y	z	U_{iso} (Å ²)
M1	0.37571 (2)	0.65381 (3)	0.87979 (8)	0.00554 (2)
M2	0.37654 (3)	0.49476 (4)	0.37242 (8)	0.00790 (3)
SiA	0.27290 (4)	0.33981 (10)	0.06186 (15)	0.00432 (8)
SiB	0.47272 (4)	0.33552 (11)	0.79094 (14)	0.00437 (8)
O1A	0.18385 (11)	0.33744 (27)	0.05107 (41)	0.00619 (20)
O1B	0.56211 (11)	0.33801 (27)	0.79066 (43)	0.00657 (20)
O2A	0.31028 (13)	0.50181 (27)	0.06606 (45)	0.00759 (20)
O2B	0.43253 (13)	0.48448 (23)	0.69441 (47)	0.00674 (22)
O3A	0.30353 (12)	0.23281 (27)	-0.16765 (44)	0.00833 (22)
O3B	0.44764 (12)	0.20091 (24)	0.58968 (41)	0.00732 (20)

(1974) and Tokonami (1965), and the anomalous-scattering factors listed in Table 2 were taken from Sasaki (1984). All structural refinements and absorption and extinction corrections were carried out with the least-squares program *RADY* (Sasaki, 1987). The refinement was performed so as to minimize the residuals of the form $\sum w_i |F_{obs} - F_{cal}|^2$ with $w_i = 1$. The reflections with $F > 3\sigma(F)$ were used in the refinement. The following structure-refinement procedure was applied to obtain the final parameters: (1) based on the model of the random distribution of Co, Ni and Zn atoms between the M1 and M2 sites, a scale factor, positional and anisotropic thermal parameters and an extinction parameter were refined with the Mo K α data; (2) the site occupancies were refined with the Co and Ni absorption-edge data (for details, see §3.5); (3) structural parameters were refined with the Mo K α data using the site occupancies obtained in (2). The results are given in Table 3. The final $R = 0.036$, $wR = 0.032$, $S = 3.42$ for 2514 symmetry-independent reflections, $(\Delta/\sigma)_{max} = 0.002$, $(\Delta\rho)_{max} = 1.4$ and $(\Delta\rho)_{min} = -1.4 e \text{ \AA}^{-3}$.

3.5. Determination of site occupancies

First, we examined the convergence and credibility of a site-occupancy refinement in the ternary system. By least-squares calculations on Co and Ni K absorption-edge data, the residual factor was obtained as a function of the occupancy of Co, Ni

and Zn atoms in the M1 sites. During these calculations, the positional and thermal parameters were fixed at the values obtained from the Mo K α data set. The triangle diagram in Fig. 1 displays iso-valued contours of the residual factor *versus* three chemical components. Each contour line is nearly parallel and

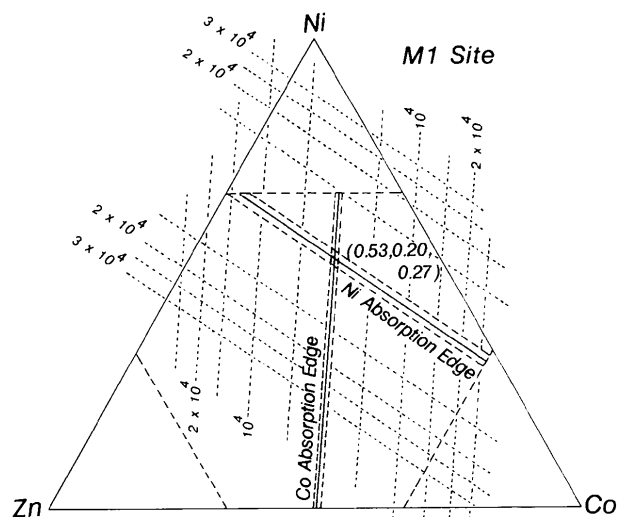


Fig. 1. Residual factor as a function of the chemical composition of the M1 site in (Co,Ni,Zn)SiO₃ pyroxene is shown in a Co-Ni-Zn triangle diagram. The composition with the minimum residual factor is expressed as a line for each data set. The most probable distribution is at the intersection of the lines.

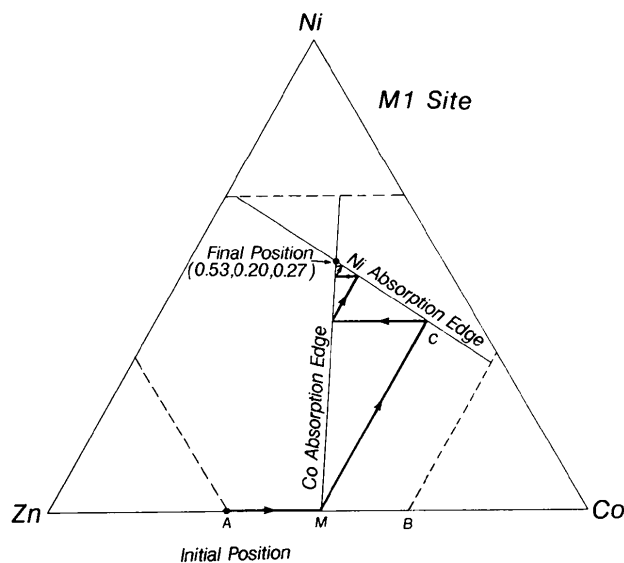


Fig. 2. Procedure to determine the M1 site occupancy. Starting from point A, the Zn/Co distribution was refined with the Co absorption-edge data, then the Zn/Ni distribution was refined with the Ni absorption-edge data (point C). This was repeated until the composition of the M1 site converged.

Table 4. *Orthopyroxene* (Co,Ni,Zn)SiO₃: occupancy parameters

The values are expressed in three figures so that total occupancy of each site becomes unity, which makes it easy to calculate the average ionic radius.

	Co	Ni	Zn
M1	0.273 (14)	0.530 (18)	0.197 (12)
M2	0.394 (14)	0.137 (18)	0.469 (12)

straight in the diagram and there is only one minimum between any two chemical components. The diagram shows an approximate position of the most probable site occupancy, and is useful in determining the procedure for obtaining the exact position.

The procedure to determine the exact site occupancy is:

(1) The Co/Zn ratio was refined using the Co absorption-edge data. Starting from point *A* in Fig. 2, we obtained a minimum of residual factors at point *M*.

(2) The Ni/Zn ratio was refined using the Ni absorption-edge data. Starting from point *M*, we obtained a minimum of residual factors at point *C*.

(3) The refinements of the Co/Zn ratio with the Co absorption-edge data, then the Ni/Zn ratio with the Ni absorption-edge data, were repeated until the occupancies converged. We finally obtained a Co:Ni:Zn ratio of 0.273 (14):0.530 (18):0.197 (12) in the *M1* sites.

4. Results and discussion

Table 3 shows the positional and isotropic thermal parameters; the anisotropic thermal parameters, which were refined with Mo *K* α data, have been deposited.* Table 4 lists the occupancy parameters in the *M1* and *M2* sites. Table 5 shows the bond lengths and angles, and Fig. 3 shows part of the crystal structure. The $F_o - F_c$ values have been deposited.*

Our experiment shows that a ternary-system cation distribution including cations close in atomic number cannot be determined with one set of intensity data even if the anomalous-dispersion effect is employed. In fact the minimum residual factor of Co or Ni absorption-edge measurement was expressed as a straight line (Fig. 1). Because each point on the line has the same probability, we cannot determine the most probable distribution.

To solve such a problem we have collected two sets of intensity data measured at two different wavelengths employing the anomalous-dispersion effect;

* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52846 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 5. *Orthopyroxene* (Co,Ni,Zn)SiO₃: bond lengths and angles

Length (Å)		Angle O—M—O (°)	Length (Å)		Angle O—M—O (°)
M1 octahedron			M2 octahedron		
M1—O1A	2.031 (2)		M2—O1A'	2.078 (2)	
—O1A'	2.158 (2)		—O1B'	2.048 (2)	
—O1B	2.060 (2)		—O2A	2.004 (2)	
—O1B'	2.184 (2)		—O2B	1.967 (2)	
—O2A	2.050 (2)		—O3A	2.435 (2)	
—O2B	2.070 (2)		—O3B	2.626 (2)	
Mean	2.092		Mean	2.193	
O1A—O1A'	3.039 (3)	93.0 (1)	O1A'—O1B'	2.845 (3)	87.2 (1)
—O1B'	2.836 (1)	84.5 (1)	—O2A	2.910 (3)	91.0 (1)
—O2A	3.047 (3)	96.6 (1)	—O2B	2.751 (3)	85.7 (1)
—O2B	2.751 (3)	84.3 (1)	—O3A	3.712 (3)	110.5 (1)
O1A'—O1B	2.836 (3)	84.5 (1)	O1B'—O2A	2.828 (3)	88.5 (1)
—O1B'	2.845 (3)	81.9 (1)	—O2B	2.987 (3)	96.1 (1)
—O2A	2.995 (3)	90.8 (1)	—O3B	3.300 (3)	88.9 (1)
O1B—O1B'	3.045 (3)	91.6 (1)	O2A—O3A	2.514 (3)	68.2 (1)
—O2A	2.828 (3)	87.0 (1)	—O3B	3.088 (3)	82.5 (1)
—O2B	3.120 (3)	98.1 (1)	O2B—O3A	3.583 (3)	108.5 (1)
O1B'—O2B	3.154 (3)	95.7 (1)	—O3B	3.573 (3)	101.2 (1)
O2A—O2B	2.956 (3)	91.7 (1)	O3A—O3B	2.927 (3)	70.6 (1)
Mean	2.954		Mean	3.085	
SiA tetrahedron			SiB tetrahedron		
SiA—O1A	1.623 (2)		SiB—O1B	1.628 (2)	
—O2A	1.597 (2)		—O2B	1.598 (2)	
—O3A	1.650 (2)		—O3B	1.659 (2)	
—O3A'	1.630 (2)		—O3B'	1.657 (2)	
Mean	1.625		Mean	1.636	
O1A—O2A	2.730 (3)	116.0 (1)	O1B—O2B	2.743 (3)	116.5 (1)
—O3A	2.701 (3)	111.3 (1)	—O3B	2.634 (3)	106.5 (1)
—O3A'	2.631 (3)	108.0 (1)	—O3B'	2.627 (3)	106.2 (1)
O2A—O3A	2.514 (3)	101.5 (1)	O2B—O3B	2.601 (3)	106.0 (1)
—O3A'	2.693 (3)	113.2 (1)	—O3B'	2.657 (3)	109.5 (1)
O3A—O3A'	2.627 (1)	106.5 (1)	O3B—O3B'	2.752 (1)	112.2 (1)
Mean	2.649		Mean	2.669	

one wavelength used is close to Co *K* edge and the other close to Ni *K* edge. Because the scattering factors of Co, Ni and Zn for Co *K* edge data are different from those for Ni *K* edge data, the lines showing minimum residual factors for Co and Ni *K* edge data have different trends. The intersection of the two lines shows the most probable distribution.

This study has determined a ternary-system cation distribution by a successive approximation method. The Co absorption-edge data refined the Co/Zn ratio while the Ni absorption-edge data refined the Ni/Zn ratio. We repeated these two refinements alternately

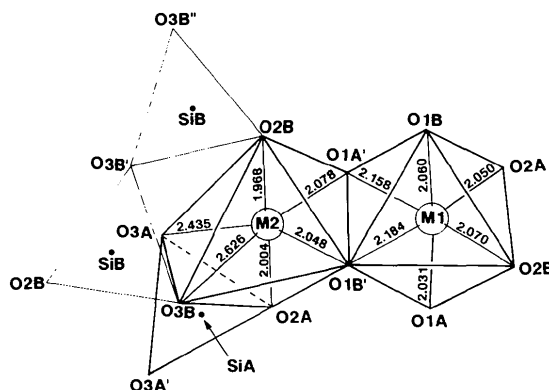


Fig. 3. Part of the structure of (Co,Ni,Zn)SiO₃ projected on (100).

to obtain the final result. We adopted this method because we could use a conventional refinement program. If a program handling two or more sets of intensity data had been available, we could have simultaneously refined the Co/Zn and Ni/Zn ratios.

Even where the atomic numbers of the cations are considerably different, the two-wavelength anomalous-dispersion method would be useful for determining ternary-system cation distributions. One set of intensity data measured at a certain wavelength may determine a ternary-system cation distribution to some extent, but the errors would be large. To reduce the errors, two sets of intensity data measured at two different wavelengths using the anomalous-dispersion effect need to be collected.

Our two-wavelength method may be extended to other combinations such as neutron and X-ray diffraction. This combination is effective for determining a ternary-system cation distribution because the atomic scattering factors for neutron diffraction are different from those for X-ray diffraction. Mössbauer spectroscopy in combination with X-ray diffraction could also be used to determine a ternary-system cation distribution if the system includes iron. These two independent methods are effective for a ternary system.

The atoms (Co, Ni and Zn) in the *M*1 or *M*2 sites should have different positions from each other, because these sites are general positions. If we have four sets of intensity data (e.g. Co, Ni and Zn absorption edges, and Mo *K* α data), we can refine the positional parameters of each atom. Sasaki & Tsukimura (1987) reported such a procedure to determine the positional parameters of each atom in (Co,Ni,Zn)SiO₃ pyroxene.

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Structure of Pb₅Cr₃F₁₉ at 295 K, Polarization Reversal and the 555 K Phase Transition

BY S. C. ABRAHAMS

AT&T Bell Laboratories, Murray Hill, NJ 07974, USA, and Institut für Kristallographie der Universität Tübingen, Charlottenstrasse 33, D-7400 Tübingen, Federal Republic of Germany

J. ALBERTSSON AND C. SVENSSON

Inorganic Chemistry 2, Chemical Center, University of Lund, S-221 00 Lund, Sweden

AND J. RAVEZ

Laboratoire de Chimie du Solide du CNRS, 351 cours de la Libération, F-33405 Talence CEDEX, France

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Abstract

Lead chromium fluoride, Pb₅Cr₃F₁₉, with $M_r = 1552.9$ is a new material with ferroelectric attributes that crystallizes in the tetragonal system. At $T = 295$ K, the space group is *I4cm* with $a = 14.384$ (5) and $c = 7.408$ (2) Å, $V = 1532.8$ (7) Å³, $Z = 4$, $D_m = 6.67$ (5), $D_x = 6.729$ g cm⁻³. For $\lambda(\text{Mo } K\alpha) =$

0.71073 Å, $\mu = 57.33$ mm⁻¹. $F(000) = 2612$. The material undergoes a first-order phase transition at 555 K. The structure was determined from 7599 (1410 independent) $F_m^2 \geq 4\sigma(F_m^2)$ with $(\sin\theta)/\lambda \leq 1.029$ Å⁻¹; least-squares refinement on wF_m^2 led to $R(F_m) = 0.044$ with $R_{\text{ini}}(F_m) = 0.040$. No atom is more than 0.72 Å from the hypothetical paraelectric state, hence the crystal is structurally ferroelectric.

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