Use of a Standard Reference Material for Precision Determination of Lattice Constants of Tetragonal Crystals

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ABSTRACT. In X-ray diffractometry, precision lattice constant determination requires corrections to the measured 2θ-angles for instrumental, sample-dependent and random errors. The external standard method could correct for instrumental errors while the analytical least squares method could eliminate other sources of errors. It was, therefore, suggested that to obtain higher accuracy the externally calibrated 2θ-values should be refined by the analytical method. When applied to X-ray diffractometric data from Cu Al_2 powder material (θ-phase) which has a tetragonal crystal structure, the lattice constants a_o and c_o were obtained as 0.60675 ± 0.00011 and 0.48775 ± 0.00006 nm, respectively.

The internal standard method could correct for systematic errors. To minimize random errors, least squares formulae were developed for the tetragonal system. When applied to the internally calibrated 2θ-values of Cu Al_2, the lattice constants a_o and c_o were obtained as 0.60695 ± 0.00010 and 0.48725 ± 0.00009 nm, respectively.

The weighted average values of the lattice constants of $CuAl_2$, at 298 K, corrected for most aberrations to peak positions were estimated as 0.60686 ± 0.00007 and 0.48760 ± 0.00005 nm. These values were considered as refinements of earlier published data.

In X-ray powder diffractometry, the lattice spacings (d) of the diffracting planes are related to the diffraction angle (2θ) and the wavelength (λ) by Bragg's law. If measurements of several different interplaner spacings were made, the lattice constants could be obtained from the known relations between interplanar spacing, Miller indices and lattice parameters. In practice, however, the measured constants are not accurate and suffer from both systematic aberrations and statistical random errors (Wilson 1980).

To calibrate the measured 2θ-angles, a standard reference material (SRM 640a) has been produced and certified (Hubbard 1983a) by the US National Bureau of Standards (NBS). The standard can be mixed with the sample to be studied (an internal standard) or used independently (an external standard) (Hubbard 1980). The objective of the present contribution was to investigate the use of the standard calibration substance for precision determination of lattice constants for materials of tetragonal crystal structures.

Materials and Methods

For X-ray diffraction, a Philips automated X-ray diffractometer was used with a PW 1710 control system, filtered Cu Kα radiation and a crystal monochromator. The working conditions were 40 kV and 30 mA for the X-ray tube, scan speed 0.03°/sec. and recorder speed 10 mm/degree. For each peak on the diffraction pattern, the 2θ-angle was measured by parabola fitting to five points around the top and was recorded to three decimal places. The temperature of the specimen was measured to 0.1 K.

The Si powder standard (SRM 640a) was used as an external and an internal 2θ calibrant for precision determination of the lattice constants of a high purity (99.999%) material. The material, known as the θ-phase, plays an important role in determining the properties of Al-Cu alloys (Mondolfo 1976) and has a tetragonal crystal structure. The particle size of the $CuAl_2$ material was about the same as that of the standard, being ∼ 10 μm.

Results and Discussion

External Standard Method

X-ray diffractograms were recorded from the Si standard and from the $CuAl_2$ material, at 304 K and 303.8 K, respectively. The lattice constant of the standard, at 298 K, was certified as 0.5430825 ± 0.0000036 nm (Hubbard 1983b). Knowing the thermal expansion coefficient of Si, the constant was corrected to the temperature of the experiment. The expected $2θ_{calc}$ values for Si were then calculated and an external calibration curve was plotted between $\triangle 2θ$ ($=2θ_{obs} - 2θ_{calc}$) and $2θ_{obs}$. The correction values $\triangle 2θ$ varied between −0.060 and +0.010° for the different peaks. This curve was used to calibrate the observed 2θ-values for $CuAl_2$. The amount of correction varied between −0.053 and +0.005°.

With X-ray diffractometers, the most important sources of systematic aberrations (Wilson 1980) arise from the sample and the instrument. Sample-dependent errors are caused by the displacement of the specimen surface from the

goniometer axis and from the absorption of X-rays in the specimen, while instrumental errors can be caused by misalignment and miscalibration of the instrument. The external standard method could correct for instrumental errors but could not correct for sample-dependent systematic errors and random errors (Razik 1987). Analytical least squares methods (Razik 1985a,b and c, and Razik *et al.* 1987) have been developed for X-ray diffractometry, to correct the measured lattice constants for sample-dependent systematic errors and for random errors.

Applying the analytical method to the calibrated 2θ-values, the best estimates of the lattice constants of $CuAl_2$ were calculated. Using the value of the thermal expansion coefficient of $CuAl_2$ (Mondolfo 1976), the lattice constants of this material, at a standard temperature of 298 K, were estimated as:

$$a_o = 0.60675 \pm 0.00011 \text{ nm}$$
$$b_o = 0.48775 \pm 0.00006 \text{ nm}$$

Internal Standard Method

The $CuAl_2$ powder was mixed intimately with an equal amount of the standard material and an X-ray diffractogram was recorded from the mixture at 304 K. An internal calibration curve was then plotted for Si and was used to calibrate the observed 2θ values for $CuAl_2$.

The internal standard method could correct for systematic errors but could not correct for random errors. When only random errors are considered, it can be shown that the correcting formulae for the tetragonal system (Razik 1985c) are reduced to:

$$B_1 = \frac{1}{\triangle} (\Sigma x_{1i} \ y_i \ \Sigma x_{2i}^2 - \Sigma x_{2i} \ y_i \ \Sigma x_{1i} \ x_{2i}) \qquad \ldots (1)$$

$$B_2 = \frac{1}{\triangle} (\Sigma x_{2i} \ y_i \ \Sigma x_{1i}^2 - \Sigma x_{1i} \ y_i \ \Sigma x_{1i} \ x_{2i}) \qquad \ldots (2)$$

where,

$$\triangle = \Sigma x_{1i}^2 \ \Sigma x_{2i}^2 - (\Sigma x_{1i} \ x_{2i})^2$$

$$x_{1i} = h_i^2 + k_i^2, \ x_{2i} = \ell_i^2, \ y_i = \sin^2 \theta_i, \ B_1 = \lambda^2/4a_0^2, \ B_2 = \lambda^2/4c_0^2$$

The uncertainties in the lattice constants can be estimated from:

$$\sigma_{a_0}^2 \simeq \frac{\lambda^2}{16 \; B_1^3} \; \frac{\Sigma \; x_{2i}^2 \; \Sigma \; \epsilon_i^2}{\Delta \; (N \, - \, 2)} \qquad \qquad \dots (3)$$

$$\sigma_{c_0}^2 = \frac{\lambda^2}{16 \; B_2^3} \; \frac{\Sigma \; x_{1i}^2 \; \Sigma \; \epsilon_i^2}{\Delta \; (N \, - \, 2)} \qquad \qquad \dots (4)$$

where,

$$\epsilon_i \; = \; y_i \; - \; B_1 \; x_{1i} \; - \; B_2 \; x_{2i}$$

When these formulae were applied to the internally calibrated 2θ-values, the best estimates of the lattice constants of $CuAl_2$, at 298 K, were calculated as:

$$a_0 \; = \; 0.60695 \; \pm \; 0.00010 \; nm$$

$$c_0 \; = \; 0.48725 \; \pm \; 0.00009 \; nm$$

Weighted Average Constants

The weighted average values (Taylor 1982) of the lattice constants of $CuAl_2$, at 298 K, were estimated as::

$$a_0 \; = \; 0.60686 \; \pm \; 0.00007 \; nm$$

$$c_0 \; = \; 0.48760 \; \pm \; 0.00005 \; nm$$

For higher accuracy, the above results must include the uncertainties in the lattice constants of the standard and in the wavelength. The relative uncertainty in the lattice constant of the standard σ_{a_s}/a_s is $\simeq 6.6 \times 10^{-6}$ and that in the wavelength used σ_λ/λ is $\simeq 5 \times 10^{-6}$ (Razik 1987). Combining these values with the values of σ_{a_0}/a_0 and σ_{c_0}/c_0, it can be shown that the total uncertainty (Taylor 1982) in the lattice constants a_0 and c_0 are 0.000070 and 0.000050 nm, respectively. A simple comparison may show that both σ_{a_s}/a_s and σ_λ/λ are much smaller than the relative uncertainties in the constants and, hence, could not affect their accuracy.

Table 1. X-ray powder diffraction data for $CuAl_2$

d (nm)	I/I_1	hkl	d (nm)	I/I_1	hkl
0.4291	100	110	0.1186	10	422
0.3034	34	200	0.1178	4	431
0.2371	60	211	0.1173	7	114
0.2146	43	220	0.1131	6	204
0.2120	94	112	0.1098	7	521
0.1919	70	310	0.1091	4	413
0.1901	77	202	0.1073	9	440
0.1611	14	222	0.1070	10	512
0.1517	4	400	0.1060	4	224
0.1508	13	312	0.1041	4	530
0.1409	16	411	0.1029	13	314
0.1394	22	213	0.1011	4	600
0.1357	15	420	0.0926	3	523
0.1288	19	402	0.0918	6	215
0.1234	23	332	0.0907	7	424
0.1219	12	004	0.0893	6	622
0.1190	9	510			

The weighted average values of the lattice constants can be considered as refinements of earlier published data reported in the JCPDS card for $CuAl_2$ (1973), being 0.6063 and 0.4872 nm for a_o and c_o, respectively, without uncertainty determination and the temperature was not mentioned. The powder diffraction data for $CuAl_2$ are listed in Table 1. The lattice spacing were calculated from the refined constants and the relative intensities were obtained by parabolic fitting without background subtraction.

Acknowledgement

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استخدام مادة قياسية لتعيين الثوابت البلورية بدقة للبلورات الرباعية

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عند استخدام حيود الأشعة السينية لتعيين الثوابت البلورية بدقة، يلزم تصحيح الزوايا المقاسة من الأخطاء الناجمة عن الجهاز والأخطاء التي تعتمد على العينة والأخطاء العشوائية، وباستخدام طريقة المعايرة الخارجية يمكن تصحيح الأخطاء الناجمة عن الجهاز فقط، وباستخدام الطريقة التحليلية لأقل المربعات يمكن تصحيح المصادر الأخرى للخطأ، ولذلك فقد اقترحنا استخدام الطريقة التحليلية لتصحيح الزوايا المعايرة للحصول على دقة أعلى في النتائج ـ وبتطبيق ذلك على نتائج حيود الأشعة السينية من مادة ألومينات النحاس ذات التركيب البلوري الرباعي كانت قيم الثوابت البلورية لها 0.60675 ± 0.00011 ، 0.48775 ± 0.00006 نانومتر.

وباستخدام طريقة المعايرة الداخلية يمكن تصحيح الأخطاء المنتظمة فقط، ومن طريقة أقل المربعات أمكن استنتاج معادلات لتصحيح الأخطاء العشوائية بالنسبة للنظام الرباعي في البلورات، وبتطبيقها على الزوايا المعايرة لمادة ألومينات النحاس كانت قيم الثوابت البلورية لها 0.60695 ± 0.00010 ، 0.48725 ± 0.00009 نانومتر، وقد قدرت القيم المتوسطة للثوابت البلورية لمادة ألومينات النحاس عند درجة 298 كلفن 0.60686 ± 0.00007 ، 0.48760 ± 0.00005 نانومتر، وأعتبرت تلك القيم بمثابة تصحيح للقيم المنشورة للمادة.