American Mineralogist, Volume 67, pages 846–847, 1982

Resolution of space group ambiguities in minerals

G. M. LOIACONO, G. KOSTECKY

Philips Laboratories
Briarcliff Manor, N.Y. 10510

AND J. S. WHITE, JR.

Smithsonian Institution
Washington, D. C. 20560

Abstract

The detection of optical second harmonic generation is a highly reliable and sensitive physical test for determination of centro and non-centrosymmetry in crystalline materials. A number of space group ambiguities reported for a selected group of minerals were resolved with a second harmonic analyzer.

Introduction

The development by Kurtz and Perry (1968) of an experimental technique to detect sound harmonic generation (SHG) in powder materials and subsequently the second harmonic analyzer (SHA) instrument of Dougherty and Kurtz (1976), permits potential resolution of space group ambiguities in numerous materials.

A number of candidates were selected from Roberts, Rapp and Weber's (1974) compilation of minerals known to have space group ambiguities. These minerals were then subjected to the testing procedures outlined by Dougherty and Kurtz (1976).

Experimental

Single crystals of each of the subject minerals were selected from the bulk samples and identification verified by X-ray diffraction. The crystals were ground into powders having a particle size between 25 to 150 μm. Approximately 5 to 10 mg of crystalline powder was then index matched using an appropriate refractive index fluid.

The apparatus was calibrated using crystalline quartz (α-SiO_2) as a powder SHG standard. The null check of the SHA was performed with an index matched KBr sample. The sensitivity for detection of second harmonic signals was 0.001 of quartz. For those samples which gave a null result, the detection sensitivity was extended to 1×10^{-4} of quartz as described by Dougherty and Kurtz (1976). All measurements were performed at 23° C.

Results and discussion

Table 1 lists the catalog number and origin of each of the mineral samples examined. The SHG measurements are summarized in Table 2. Of the nine minerals examined only three—dewindtite, fibroferrite and nasonite—gave a null result. Further measurements, at high detection sensitivity, with these minerals indicated no existence of second harmonic activity. Therefore, we conclude that these samples are truly centrosymmetric.

The relative intensity of the second harmonic signal for those minerals which gave a positive response is small in comparison to quartz. Therefore, in terms of potential device applications, these minerals are not of interest.

Table 1. Identification of minerals

MINERAL	CATALOG NOS.	ORIGIN
Alunite	R-17342	Tolfa, Roma, Laxio, Italy
Bavenite	134212	Kings Mtn., North Carolina
Benstonite	R-16603	Minerva Mine, Illinois
Corundophilite	18180	Chester, Massachusetts
Dewindtite	R-9876	Shinkolobwe, Zaire
Ephesite	138159	Postmasburg, South Africa
Fibroferrite	83601	Copiapo, Chile
Moraesite	133863	Palermo, New Hampshire
Nasonite	C-6226	Franklin, New Jersey

These minerals were obtained from the National Museum of Natural History. Smithsonian Institution.

0003–004X/82/0708–0846$02.00

Table 2. Summary of SHG data (23° C)

MINERAL	FORMULA	POSSIBLE SPACE GROUPS	SHG TEST	$I_{2\omega}$ (Rel. α SiO_2)	TRUE SPACE GROUP
Alunite	$KAl_3(SO_4)_2(OH)_6$	$R3m$, $R\bar{3}m$	+	0.008	$R3m$
Bavenite	$Ca_4(Be,Al)_4Si_9(O,OH)_{28}$	$Amma$, $Am2a$	+	0.004	$Am2a$
Benstonite	$MgCa_6(Ba,Sr)_6(CO_3)_{13}$	$R3$, $R\bar{3}$	+	0.005	$R3$
Corundophilite	$(Mg,Fe,Al)_6(SiAl)_4O_{10}(OH)_8$	$C_{2/m}$, Pi	+	0.003	$P1$
Dewindtite	$Pb(UO_2)_2(PO_4)_2 \cdot 3H_2O$	$Bmb2$, $Bmmb$	0	-	$Bmmb$
Ephesite	$Na(LiAl_2)(Al_2Si_2)O_{10}(OH)_2$	$C2/c$, C_c	+	0.03	Cc
Fibroferrite	$FeSO_4OH \cdot 5H_2O$	$R3$, $R\bar{3}$	0	-	$R\bar{3}$
Moraesite	$Be_2PO_4OH \cdot 4H_2O$	m, $2/m$	+	0.01	m
Nasonite	$Ca_4Pb_6Si_6O_{21}Cl_2$	$P6_{3/m}$, $P6_3$	0	-	$P6_{3/m}$

Acknowledgments

The authors wish to thank the National Museum of Natural History, Smithsonian Institution, Mineralogy Division for making available the mineral samples studied.

References

Dougherty, J. P. and Kurtz, S. K. (1976) A second harmonic analyzer for the detection of non-centrosymmetry. Journal of Applied Crystallography, 9, 145–158.

Kurtz, S. K. and Perry, T. T. (1968) A powder technique for the evaluation of nonlinear optical materials. Journal of Applied Physics, 39, 3798–3813.

Roberts, W. L., Rapp, G. R. and Weber J. (1974) Encyclopedia of Minerals. Van Nostrand Reinhold, New York.

Manuscript received, October 21, 1981; accepted for publication, March 16, 1982.