

## Resolution of space group ambiguities in minerals

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### 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  $\mu\text{m}$ . 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 ( $\alpha\text{-SiO}_2$ ) 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  $1 \times 10^{-4}$  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, Lacio, 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.

Table 2. Summary of SHG data (23° C)

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

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### References

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