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Optical isotropy in polycrystalline $Ba_2TiSi_2O_8$: Testing the limits of a well established concept

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We report an optical properties investigation of randomly oriented polycrystalline solids with anisotropic crystal structure. Using fresnoite as the model material, we demonstrate several domain size effects, most notably that a cross-polarization response is observed for the case of large randomly oriented crystallites. We compare our measured results with simulations from several different dielectric models and demonstrate that the appropriate model depends upon the grain size. The results have important implications for the understanding of optical isotropy in polycrystalline materials and bulk vs nanoscale effects.

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I. INTRODUCTION

If a material has no directional dependence to the optical properties, it is characterized as being "optically isotropic." This natural definition is commonly broadened to include two additional assumptions: (1) that such a material can be properly described by a scalar dielectric function and (2) that the dispersion of this dielectric function can be simulated by simple models such as the classical damped harmonic oscillator model.[1] Although they are often applied (and may even be useful in practice to extract basic information),[2,3] these assumptions have not been tested in detail for granular materials.

Infrared spectral modeling of randomly oriented mesocrystalline and microcrystalline materials from single-crystal data presents a prominent test case for the two ideas that extend the original definition of optical isotropy. This is because assumptions (1) and (2), above, dictate how the optical properties of a single crystal must be averaged in order to simulate or predict the spectral properties of related isotropic materials. Thus, various averaging schemes can be evaluated by direct comparison with experimental data. An understanding of the averaging procedure is very important for proper interpretation of the spectra of polycrystalline materials, and it is needed to extract microscopic spectral information about the material if the sample is not available in single-crystal form.

We selected fresnoite ($Ba_2TiSi_2O_8$) as a model material for our investigations because of its strong optical anisotropy in the Reststrahlen region and its availability in both single-crystal and randomly oriented mesocrystalline and microcrystalline form.[4–6] By comparing our measured spectral results with simulations from several different dielectric models, we assess the concept of optical isotropy in the infrared range. An important consequence of (1) is that the principal dielectric functions of a single crystal must be averaged in a way that a scalar dielectric function for the corresponding isotropic material is obtained. No cross-polarization effect is anticipated. Criteria (2) places certain limits on the dielectric averaging procedures, namely, that the dispersion of the single-crystal principal dielectric functions as well as the dispersion of the averaged dielectric function of the isotropic material must be described by simple models. Using fresnoite as the target compound, we find important grain size and dielectric effects which demonstrate that assumptions (1) and (2) are not generally appropriate for describing the optical properties of polycrystalline materials. Instead, we show that the scalar dielectric function for small grain materials must be based upon an appropriate average of the principal dielectric functions or indices of refraction. In the case of large grain materials, the optical model must account for the cross polarization response, reported here for fresnoite.

II. METHODS

Polycrystalline fresnoite was prepared from a stoichiometric melt of the raw materials [$BaCO_3$ (Merck), TiO_2 (Merck), SiO_2 (Schott)] at 1500 °C. Quenching of the melt led to a clear glass, which was crystallized by a 1 h heat treatment at 1000 °C, resulting in a polycrystalline material with a crystallite domain size of ~300 nm. A direct crystallization of the melt led to a partly oriented ceramic with a crystallite size of ~10 μm. The corresponding isotropic material was prepared by milling the ceramic followed by a compaction of the powder by spark plasma sintering (SPS). The ceramics were gradually polished with 6, 3, and 1 μm grain size diamond paste until an optically reflecting surface was achieved.[7] The surface quality of the SPS sample was somewhat lower compared to the crystallized glass. Both polycrystalline samples have the same density as the single crystal [4.43 g/cm^3 (Ref. 7)] within experimental error.

Room-temperature infrared reflectance spectra were measured using two different Fourier transform infrared spectrometers, a Bruker 113V and a Bruker 66, covering the frequency range between 22 and 6000 cm^{-1}. Polarization selection was obtained using both polyethylene wire grid and KRS-5 polarizers, as appropriate. Gold and aluminium mirrors served as the reference. Since the polycrystalline samples were large, a sizable beam (5 mm) was employed to

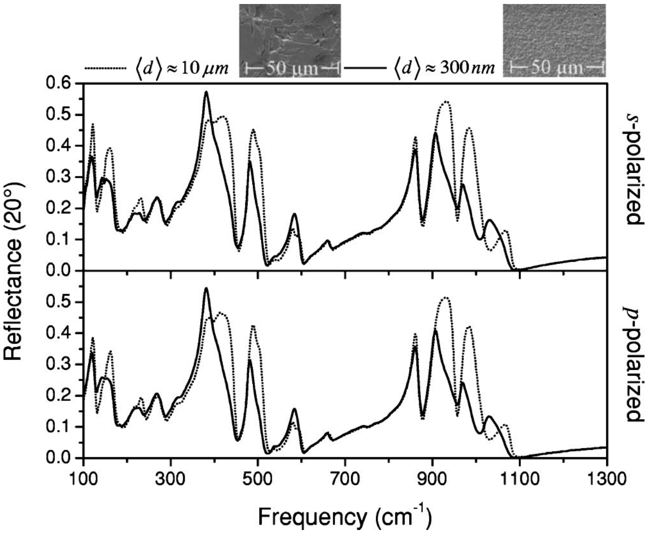

FIG. 1. 300 K infrared reflectance spectra of randomly oriented polycrystalline fresnoite with average crystallite diameters $d \approx 10$ μm and 300 nm. These data were taken with a 20° angle of incidence. Polarizer positions were set for both *s*- and *p*-polarized incident radiation; no analyzer was used. The similarity between the *s*- and *p*-polarized spectra for the small domain material is a consequence of the sample isotropy and the comparably small angle of incidence.

assure the collection of average optical properties.

To test our ideas about optical isotropy in these polycrystalline materials, we carried out simulations to model the spectral response for samples with different grain sizes. Here, it is important to note that the terms "small" and "large" are related to wavelength. For example, in the infrared, a "large" domain size is on the micron scale, whereas in the ultraviolet spectral region, a domain size bigger than 30 nm should be considered "large." To model the spectral response of polycrystalline solids consisting of small crystallites, we employed both effective medium approximation (EMA) and average refractive index theory (ARIT).[4,8–16] Both techniques use the dielectric function data of the corresponding single crystal and allow us to obtain an averaged dielectric function (or index of refraction).[2] For the case of samples with large crystallites, we used average reflectance and transmittance theory (ARTT). A detailed description of this approach is given in Refs. 5, 6, and 17.

III. RESULTS AND DISCUSSION

Understanding the infrared response of large grain fresnoites

Figure 1 shows a comparison of the infrared spectral response of two polycrystalline fresnoite samples with different domain sizes. One material consists of crystallites with an average diameter of $\sim$10 μm; the other sample has crystallites with $\sim$300 nm average diameter. Strong differences in peak position, line shape, and relative peak intensity are observed, except between about 600 and 880 cm^{-1}, where the single crystal is nearly isotropic and devoid of vibrational structure. We attribute these spectral differences to the polycrystalline size effect, which is intimately connected with the optical anisotropy of individual crystallites.[18]

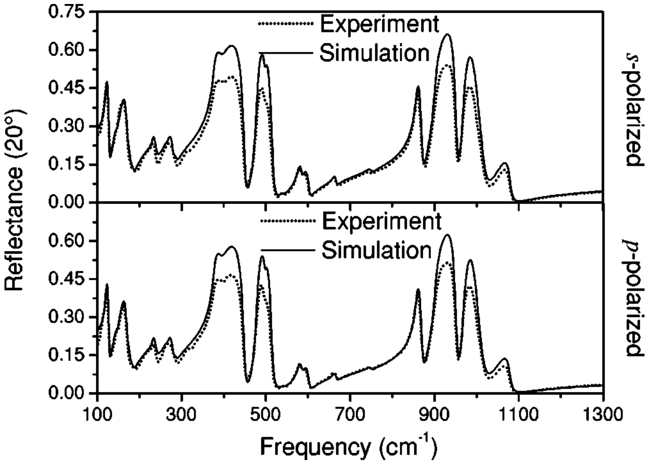

FIG. 2. Comparison of the measured *s*- and *p*-polarized reflectance spectra of large domain sized polycrystalline fresnoite with simulated results to test Doll's hypothesis (Ref. 21). A 20° angle of incidence was employed. Polarization selection (*s* or *p*) was made on the incident radiation; no analyzer was used.

Such a size effect in randomly oriented polycrystalline samples has been noticed previously. The case of polycrystalline cuprate superconductors is a good example.[19–21] Here, Doll *et al.* model the spectra of samples consisting of large crystallites by averaging the individual crystallite reflectances $R(\Omega)$, as a function of crystallite orientation Ω:

$$\langle R\rangle = \frac{1}{2}\langle R_s\rangle + \frac{1}{2}\langle R_p\rangle = N^{(3)}\int_{\Omega^{(3)}}\left(\frac{R_s(\Omega)}{2}+\frac{R_p(\Omega)}{2}\right)d\Omega. \tag{1}$$

$N^{(3)}$ is a normalization factor given by $N^{(3)}=(\int_{\Omega^{(3)}}d\Omega)^{-1}$. This approach is similar to a model proposed earlier by Frech,[22] which was validated by comparing the measured reflectance from a microcrystalline sample of NaNO$_3$ for three different angles of incidence. To test Doll's hypothesis, we simulated the spectra of polycrystalline fresnoite consisting of large crystallites based on the dielectric response of the single crystal[23] according to Eq. (1) and compared the results to the measured infrared reflectance (Fig. 2). Peak positions, band shapes, and relative intensities are in excellent agreement.[24] We therefore conclude that this approach of averaging the reflectances works well for describing the polarized reflectance of large grain size polycrystalline samples.

The ARTT model incorporates the aforementioned formalism for simulating the spectral response of a large grain polycrystalline sample by averaging the reflectances over the orientations. It also applies an exact 4×4 matrix technique developed by Yeh,[25] modified slightly to permit air or vacuum as incidence medium.[26] This approach was originally developed to facilitate modeling of dual polarizer experiments (one before and one after the sample). While simulating the results of our experiments, we noticed that Eq. (1) predicts cross-polarization terms in the reflectance $\langle R_{sp}\rangle$ and $\langle R_{ps}\rangle$. Here, the brackets denote an average response, the first

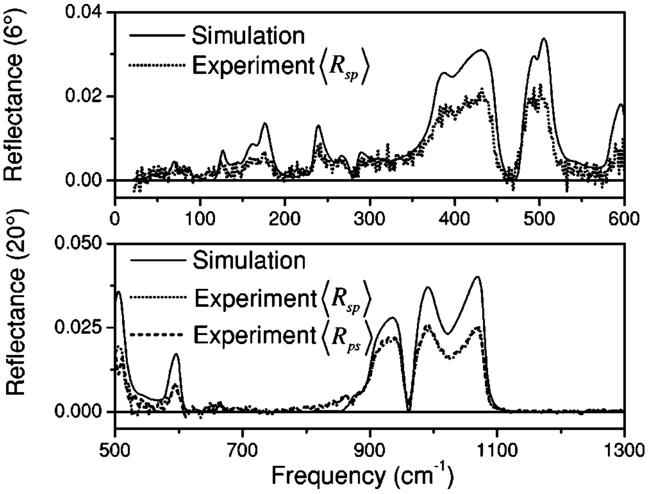

FIG. 3. A comparison of the measured and simulated cross-polarized reflectance spectra of polycrystalline fresnoite consisting of large crystallites. The angle of incidence was 6° in the far infrared, with *s*-polarized incident radiation. The angle of incidence was 20° in the middle infrared, and we show results for both *s*- and *p*-polarized incident radiation. In each case, the analyzer was orthogonal to the polarizer. Note that cross polarization effects are not observed in samples where the randomly oriented domains were small compared with the wavelength of light.

subscript indicates the orientation of the polarizer relative to the plane of incidence, and the second subscript denotes the same for the analyzer. The physical origin of this cross-polarized reflectance is interesting. The components of the reflectance, R_{sp} and R_{ps}, are zero only along the principal directions of a high-symmetry crystal and when the optical axis is contained within the plane of incidence.[24] Away from these conditions, the orientationally averaged cross polarization terms $\langle R_{sp}\rangle$ and $\langle R_{ps}\rangle$ are finite. The excellent resemblance between the experimental and simulated spectrum for the single-polarizer experiment (Fig. 2) encouraged us to carry out additional experiments with two polarizers, including those with crossed polarizers. The case of crossed polarizers[27] is of special interest, as the ARTT formalism extends the earlier work of Doll[21] and Frech[22] by separately quantifying the cross-polarization terms of a randomly oriented polydomain medium with large grain sizes.

To test these ideas, we measured the cross-polarization reflectance of both large- and small-domain polycrystalline fresnoite. Our objective was to search for, investigate, and quantify the frequency dependence of the predicted cross polarization effect. Figure 3 shows a comparison of the measured cross-polarization reflectance of large-grain polycrystalline fresnoite with the simulated spectral response. Excellent agreement is obtained, indicating that ARTT is a reasonable approach for modeling the cross polarization effect under these conditions ($\lambda < d/10$). Observation of a cross polarization response for the case of large, randomly oriented crystallites is important, as it implies that such an isotropic material cannot be characterized by a scalar dielectric function. That an isotropic solid cannot always be described by a scalar dielectric function goes to the heart of the definition of optical isotropy.[1,28]

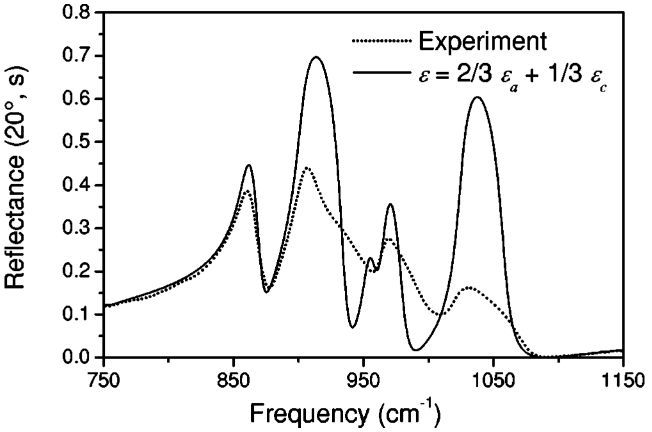

FIG. 4. Comparison of the experimental and simulated reflectance spectra of polycrystalline fresnoite consisting of small crystallites. A 20° angle of incidence and *s*-polarized incident radiation were employed for the measurements. The simulation employs a linear combination of the principal dielectric functions of the $Ba_2TiSi_2O_8$ single crystal (Ref. 4). Note the poor agreement between the two curves.

Understanding the infrared response of small grain fresnoites

What can we learn from the spectra of the isotropic material consisting of small crystallites? Since we observed no cross-polarization spectral response, such materials can indeed be described by a scalar dielectric function, as no coupling between the *s*- and *p*-polarized waves occurs.[1] The dispersion of this scalar dielectric function $\langle\varepsilon(\tilde{\nu})\rangle$ can be simulated by the classical damped-harmonic-oscillator approach[29] as

$$\langle\varepsilon(\tilde{\nu})\rangle = \sum_{i=1}^{N}\frac{S_i^{\,2}}{(\tilde{\nu}_i^{\,2}-\tilde{\nu}^2)-i\tilde{\nu}\gamma_i}+\langle\varepsilon_\infty\rangle. \qquad (2)$$

Here, oscillator position $\tilde{\nu}_i$, damping constant γ_i, and strength S_i are of special interest for spectroscopists. However, we have to keep in mind that the crystallites themselves are also optically anisotropic and that the oscillators can be distinguished according to the orientation of their transition moments relative to the crystal axes. For uniaxial fresnoite ($a=b\neq c$), we can write

$$\langle\varepsilon(\tilde{\nu})\rangle = \sum_{i=1}^{N_a}\frac{S_{\mathrm{i},a}^2}{(\tilde{\nu}_{\mathrm{i},a}^2-\tilde{\nu}^2)-i\tilde{\nu}\gamma_{\mathrm{i},a}}+\sum_{i=1}^{N_c}\frac{S_{\mathrm{i},c}^2}{(\tilde{\nu}_{\mathrm{i},c}^2-\tilde{\nu}^2)-i\tilde{\nu}\gamma_{\mathrm{i},c}} + \frac{2}{3}\varepsilon_{\infty,a}+\frac{1}{3}\varepsilon_{\infty,c} \mathrel{\hat{=}} \frac{2}{3}\varepsilon_a(\tilde{\nu})+\frac{1}{3}\varepsilon_c(\tilde{\nu}). \qquad (3)$$

Dispersion of the scalar dielectric function according to Eqs. (2,3) is equivalent to a linear mixing of the principal dielectric functions $\varepsilon_a(\tilde{\nu})$ and $\varepsilon_c(\tilde{\nu})$. If we compare the measured spectrum of a small-domain sample of polycrystalline fresnoite with the simulated response based upon Eq. (3), we find overall poor agreement, except between 600 and 880 cm^{-1}, where the fresnoite single crystal is almost isotropic anyway (Fig. 4).

The failure of this simple model raises the question of whether there are better approaches with which to describe the averaged dielectric function for small-domain sized polycrystalline materials. Indeed, there are two prominent models. The first is EMA, which has its origins in electrostatics[7–15] and is often called the quasistatic approximation.[13] Its basic assumption is that a polycrystalline medium is made up of three different constituents with principle dielectric functions ε_a, ε_b, and ε_c of the corresponding single crystal. These constituents are embedded in a hypothetically background medium with an average dielectric function, which is self-consistently determined. Therefore all constituents of the heterogeneous material are treated equally. The average dielectric function of an inhomogeneous sample $\langle\varepsilon\rangle$ is calculated from the ratio of the volume-averaged displacement field $\mathbf{D}_{\mathrm{av}}$ and the electrical field $\mathbf{E}_{\mathrm{av}}$ parallel to the applied field $\mathbf{E}_0$.[14] Extensions to the EMA account for ellipsoidal crystallite shapes in polycrystalline materials.[14,15]

For a uniaxial material with spherically shaped crystallites and full volume occupation such as fresnoite crystallized from the corresponding glass, the EMA yields

$$\frac{2}{3}\frac{\varepsilon_a-\langle\varepsilon\rangle}{\varepsilon_a+2\langle\varepsilon\rangle}+\frac{1}{3}\frac{\varepsilon_c-\langle\varepsilon\rangle}{\varepsilon_c+2\langle\varepsilon\rangle}=0, \qquad (4)$$

where

$$\langle\varepsilon\rangle_{+,-}=\frac{1}{4}(\varepsilon_a\pm\sqrt{\varepsilon_a}\sqrt{\varepsilon_a+8\varepsilon_c}). \qquad (5)$$

The positive root $\langle\varepsilon\rangle_+$ is physically relevant.

An alternative method for the calculation of effective optical constants is ARIT. This approach is similar to ARRT in that orientationally averaged optical properties are calculated. However, the refractive indices $n_1(\Omega)$ and $n_2(\Omega)$ are averaged instead of reflectance and transmittance

$$\langle n\rangle = N^{(3)}\int_{\Omega^{(3)}}\left(\frac{n_1(\Omega)}{2}+\frac{n_2(\Omega)}{2}\right)d\Omega, \qquad (6)$$

since it is assumed that the crystallites are smaller than the resolution limit of light, resulting in an averaged scalar index of refraction as required.[4] This scheme is thus slightly different from that in EMA.

We simulated the dielectric response of polycrystalline fresnoite consisting of small crystallites using both EMA and ARIT theories and compare the results with the experimental spectrum in Fig. 5. The strong resemblance between the simulated and measured spectra indicates that both EMA and ARIT are proper approaches, with slight advantages for ARIT, especially in the vicinity of the oscillators. We note that neither model contains the underlying assumption of a linear combination of the principal dielectric functions. This result shows that the dispersion of the averaged dielectric function of a randomly oriented small-grain polycrystalline material should be described by dielectric function models that embed proper averaging techniques.

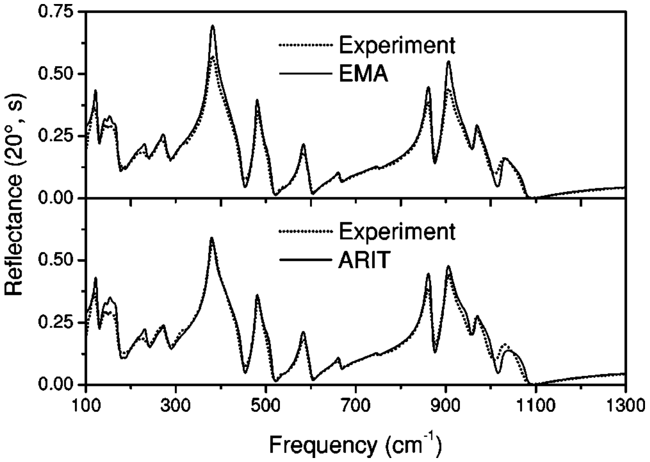

FIG. 5. Comparison of the experimental and simulated reflectance spectra of polycrystalline fresnoite consisting of small crystallites. A 20° angle of incidence was used for the measurements. Both *s*- and *p*-polarized incident radiation were employed, as appropriate. No analyzer was used. The results of two different simulation methods effective medium approximation (EMA) (upper panel) and average refractive index theory (ARIT) (lower panel), are shown for comparison.

IV. CONCLUSION

We report an optical properties investigation of randomly oriented polycrystalline materials with anisotropic crystal structure. Using fresnoite as the model material, we demonstrate several domain size effects in the infrared, although we anticipate that these findings can be extended to other frequency regimes. We find that randomly oriented polycrystalline materials with large crystallites show a sizable and frequency-dependent cross polarization response. One consequence of this observation is that such a material should not be characterized by a scalar dielectric function. For the case of a randomly oriented polycrystalline material consisting of crystallites that are small compared to the wavelength of light, there is no cross-polarization response, so the use of a scalar dielectric function is appropriate. We show, however, that a linear averaging scheme of the principal dielectric function does not describe the average dielectric function of such a material. To capture the frequency dispersion of the averaged dielectric function for small grain materials, more sophisticated models must be employed. These findings have several implications for optical properties investigations of polycrystalline materials. First, the term “optical isotropy” should be taken only to imply that there is no directional dependence to the optical properties. Further, because there are important domain size effects in polycrystalline solids, it is necessary to know the size of the ordered domains compared with the wavelength of light in order to describe the optical properties of a polycrystalline material. Finally, if a considerable fraction of the polycrystalline sample consists of large ordered domains, a Kramers-Kronig analysis or a dispersion analysis may not be applicable since no average dielectric function exists.[30] Taken together, domain size effects in polycrystalline materials may hold interesting surprises as well as opportunities for control and manipulation of light.

ACKNOWLEDGMENTS

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[18] We have also performed x-ray-diffraction and x-ray-goniometry measurements on the samples (Refs. 2–4). According to these measurements the samples are single phased, consist of the same phase and are randomly oriented. Therefore we can exclude partial ordering or the existence of different structural modifications from causing the spectral differences.

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[26] The formalism originally introduced by Yeh cannot be applied if the dielectric tensor of one medium (e.g, the incidence medium) is a scalar. However, the 4×4 matrix of such a medium can be derived easily (Ref. 5).

[27] Here, orientations of the polarizer are of special interest, where they are crossed, but parallel and perpendicular to the plane of incidence.

[28] Note that the excellent resemblance between simulated and measured spectra proves that coherence or interface effects do not contribute strongly to the measured reflectance, since it is straightforward to show that an average of the amplitudes leads to zero cross polarization. The overall resemblance between model and experiment is also considerably reduced if such effects are considered. We therefore conclude that they play no important role, at least in the case of polycrystalline fresnoite.

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[30] Applying a Kramers-Kronig analysis or a dispersion analysis to spectra stemming from polycrystalline large grain material, the so-obtained maxima of the imaginary part of the pseudodielectric function do not correspond to oscillator frequencies of the corresponding single crystal in general, but are shifted towards higher wave numbers. Depending on the TO-LO splitting this shift can easily exceed, e.g., the 35 cm^{-1} found for the high wave number absorption of fresnoite at 1025 cm^{-1}. Further, apart from the impossibility to predict the results of experiments carried out with polarizer and analyzer, it is not permitted to use the pseudodielectric function to compute spectra at arbitrary angles of incidence.