Electrical and mechanical properties of samarium barium copper oxalate crystals

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Samarium barium copper oxalate (SmBaCuOx) crystals were grown using silica gel technique by the diffusion of a mixture of samarium chloride, barium chloride and cuprous nitrate into the test tube having the set gel containing oxalic acid. The grown crystals were characterized by X-ray diffraction analysis, Inductively Coupled Plasma Atomic Emission analysis and microhardness measurements. The variation of dielectric constant \(\varepsilon\) and dielectric loss \(D\) in the frequency range 100Hz - 1MHz has been studied and reported. The electrical conductivity of SmBaCuOx crystals was found to increase with increase of frequency.

Keywords: Samarium barium copper oxalate crystals, Inductively coupled plasma emission system, Electrical conductivity, Microhardness

1 Introduction

Crystal growth is a heterogeneous chemical process in which conversion from one phase to another phase of a compound is involved. In the field of crystal growth, gel technique has become more popular and has been used by several researchers\textsuperscript{1,2}. It can be successfully used at room temperature to suppress nucleation centre\textsuperscript{3} and is suitable for crystals having low solubility\textsuperscript{4}.

Rare earth compounds have a significant place among the technologically important materials. They have their importance for the luminescent, photoconductive, photorefractive, laser action, electric, magnetic and superconducting properties\textsuperscript{5}. The rare earth oxalates evoked greater attention because of their ionic conduction and their easy conversion into their corresponding oxides\textsuperscript{6,7}. Synthesis of superconducting compounds by the controlled precipitation of oxalates followed by calcinations has been reported\textsuperscript{8}. The ferroelectric and ferro elastic properties of rare earth molybdates and oxalates find applications in electro and acousto optical device\textsuperscript{9}. The rare earth doped lasers is quite suitable for pulse generation with \(Q\)-switching\textsuperscript{10}.

2. Experimental Details

The gel was prepared by mixing sodium meta silicate (density=1.03 g/cc) with oxalic acid to obtain the desired \(pH\) value. A mixed solution of samarium chloride, barium chloride, cuprous nitrate and nitric acid was used as the outer electrolyte. The outer electrolyte diffused into the gel to form a colloidal precipitate and it was dissolved by nitric acid which enhanced crystallization.

\[
2\text{SmCl}_3\cdot 6\text{H}_2\text{O} + \text{Cu(NO}_3)_2 \cdot 3\text{H}_2\text{O} + \text{Ba Cl}_2\cdot 2\text{H}_2\text{O} + 5\text{H}_2\text{C}_2\text{O}_4\cdot 2\text{H}_2\text{O} \rightarrow \text{Sm}_3\cdot \text{Ba Cu (C}_2\text{O}_4)_5 \cdot 9\text{H}_2\text{O} + 8 \text{HCl} + 18\text{H}_2\text{O} + \text{2HNO}_3
\]

3 Results

3.1. X-ray analysis

In order to estimate the crystal data, X-ray diffraction was carried out using Bruker AXS D8 Advance X-ray Diffractometer with CuKa radiation \(\lambda=1.54180\AA\). The SmBaCuOx crystals were indexed in tetragonal symmetry using a computer program called Powder Diffraction Package (PDP-11). The lattice parameters were:

\(a=b=15.430\) and \(c=10.019\) \(\AA\)

3.2. Analysis using inductively coupled plasma atomic emission spectrometer

The atomic spectrum emitted by the sample is used to determine its elemental composition by Inductively Coupled Plasma Atomic Emission Spectrometer (ICP – AES). The wavelength at which emission occurs identifies the element, while the intensity of the...
emitted radiation quantifies its concentration. The result of the analysis is presented in Table 1.

3.3 Electrical conductivity of samarium barium copper oxalate crystals

The rare earth compounds have attracted considerable attention on the account of their interesting electric properties like conductivity. The dielectric constant ($\varepsilon_r$) and loss tangent (tan$\delta$) were obtained as a function of frequencies (100Hz-1MHz) at room temperature by an Impedance Analyzer Hewlett Packard (Japan) HP4192A and is plotted in Fig. 1 (a and b). It is observed that both dielectric constant and loss tangent show similar variation with frequency. The dielectric constant and the dielectric loss are both inversely proportional to frequency (Fig. 1). This is a normal dielectric behaviour that both dielectric constant and the dielectric loss decrease with increasing frequency. This can be understood on the basis that the mechanism of polarization is similar to that of the conduction process. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. As the frequency increases, a point will be reached where the space charge cannot sustain and comply with the external field. Hence, the polarization decreases, giving rise to diminishing values of dielectric constant and the dielectric loss$^{11}$.

Table 1—Elemental composition of SmBaCuOx crystals

<table>
<thead>
<tr>
<th>Elements</th>
<th>Average</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barium</td>
<td>7.191%</td>
<td>%</td>
</tr>
<tr>
<td>Copper</td>
<td>0.233%</td>
<td>%</td>
</tr>
</tbody>
</table>

Fig. 1 (a) — Frequency dependence of dielectric loss of SmBaCuOx

Fig. 1(b) — Frequency dependence of dielectric constant of SmBaCuO$_x$

Fig. 2 — Log $f$ versus conductivity (B= -24°C, C= -10°C, D= 0°C, E= 5°C, F= 30°C, G= 35°C)

Fig. 3 — Load $P$ versus $Hv$ graph for SmBaCuO$_x$
The electrical conductivity of SmBaCuO₅ crystals was determined at various temperatures and frequencies. Log\(f\) versus electrical conductivity at various constant temperatures (-24°, -10°, 0°, 5°, 28° and 35°C) is plotted in Fig. 2 which reveals that electrical conductivity increases with increase of frequency and temperature.

3.4 Microhardness

Hardness of SmBaCuO₅ crystals was determined using Vickers pyramidal indenter for various loads. Hardness number of the crystal is calculated using the relation:

\[ H_v = 1.8544 \frac{P}{d^2} \text{kg/mm}^2 \]

where \(P\) is the applied load in kg and \(d\) is the average diagonal length of the indented impression in millimeter. Fig. 3 shows the Vickers hardness profile as a function of applied load.

In the present paper, the hardness number of SmBaCuO₅ crystals was found to increase with increase in load, confirming the hardness property of the crystal.

The work hardening coefficient, \(n\), from the slope (higher load region) of log \(P\) versus log \(d\) using least square fit method has been determined. The value of \(n\) was found to be greater than 2. According to Onitsch.'s\(^\text{12}\) theory, if \(n\) is greater than 2, the materials are said to be soft ones. Samarium barium copper oxalate crystals grown in the present study fall in the category of soft materials.

4 Conclusions

Precipitation-cum-dissolution control mechanism of the growth of rare earth mixed crystals is a useful method for growing good quality crystals. Dielectric studies reveal the suitability of SmBaCuO₅ for high SHG efficiency. From microhardness measurements, we conclude that the grown crystals belong to soft materials.

References

10 www rp-photonics com- rare_earth_doped_gain_media.html.