Phase-Change Sintering of BaCl₂ Transparent Ceramics

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We report on the compaction of anhydrous BaCl₂ powders under severe plastic deformation and the conversion of their native orthorhombic cotunnite crystalline structure into a fine-grained cubic fluorite structure. This conversion, supported by x-ray diffraction and transmission electron microscopy data, and which enables the production of highly dense ceramics of BaCl₂, occurs 500°C below the known phase transition temperature of 925°C for this material at 1 atm. We discuss this phase change in the context of a stress-induced polymorphic transformation and its implication on the fabrication of transparent ceramics for scintillator applications.

Keywords: martensitic transformation, transparent ceramics, severe plastic deformation

1. Introduction

A variety of halide materials can be formed into transparent polycrystalline ceramics by powder compaction at room or mild temperatures. Such process is typically used in the fabrication of infrared-transmissive optics, including MgF₂ windows [1–3] and KBr substrates for Fourier-Transform Infrared (FTIR) spectroscopy, and has been investigated for the production of CaF₂ laser host media [6] and scintillator materials, such as CsI, SrI₂, and LaBr₃[4,5,7]. In this technique, the densification of powder compacts proceeds through the deformation of individual crystallites brought about by the plastic yield of preferentially-oriented crystallographic planes with respect to the direction of the local state of stress. The microstructure of the pressed ceramics is greatly altered by the deformation (development of texture, shear bands), and may undergo significant amount of recrystallization (microstructure refinement) if large levels of stress are applied. These effects are exemplified in the so-called Severe Plastic Deformation

(SPD) techniques, introduced a few decades ago in metallurgy for the production of high-strength metals and alloys by Equal Channel Angular Pressing (ECAP), High-Pressure Torsion (HPT), asymmetric rolling or mechanical milling of powdered samples[8]. In the same way, uniaxial forging of non-metallic single-crystals, in which unconstrained lateral plastic deformation is produced, has been successfully applied to the production of fine-grained polycrystalline optical materials with higher mechanical strength, toughness and enhanced plastic behavior over the single-crystalline form[9,10].

Large states of stress however can bring additional effects such as those observed in oxide polymorphs related through diffusionless martensitic-like phase transformations. In 1970, Coe reported that the so-called “thermodynamic effect of shear stress” causes a significant shift in the orthorhombic-to-monoclinic transformation temperature (on the order of -3°C per MPa) in the enstatite mineral MgSiO_3 [11,12]. In the single-crystal form, this temperature shift, ΔT , was found to be in good agreement with a shear stress Clausius-Clapeyron analog: $\Delta T = \frac{\gamma_{\alpha\beta}}{S_{\alpha\beta}} \tau$, where $S_{\alpha\beta}$ stands for the variation in entropy at the phase transition, $\gamma_{\alpha\beta}$ the value of the transformation shear strain and τ the resolved external shear stress [13]. In ceramics, a few examples of shear-induced displacive transformations are known, the most notable of which being the stress-activated tetragonal-to-monoclinic transition in zirconia (ZrO_2), finding use in toughness enhancement of ceramics[14,15]. Recently, a disordered hexagonal-to-wurtzite phase transition in a rotational diamond anvil cell has been shown to occur at pressures 45 GPa lower than previously reported under hydrostatic conditions[16]. What is more, the phase reversion which naturally occurs upon cooling and pressure release can be inhibited in fine-grained polycrystalline samples because of the excess free-energy associated to the large fraction of grain-boundaries, the strain from the randomly-oriented surrounding crystallites, and the lack of suitable nuclei to initiate the transformation [17–19].

In this study, we show that the combined effects of stress-intensification and stress-induced phase change during the compaction of orthorhombic barium chloride (o- BaCl_2) powders can be leveraged to produce fine-grained transparent ceramics of cubic barium chloride (c- BaCl_2), 500°C below the known transition temperature of 925°C. Additionally, we show that this metastable cubic phase is stable at room temperature and up to 300°C. This is realized under conditions created in a custom-designed hot-pressing

apparatus[20].

2. Materials and Methods

High purity anhydrous o-BaCl₂ powders (99.999% metals basis, Sigma Aldrich) were ground and sieved to achieve a particle size in the range 75 to 150 μm . These powders were then pre-compacted at 3 MPa into 13 mm-diameter pellets. These pellets were loaded into a 25-mm diameter floating stainless steel die assembly and surrounded by 75 – 150 μm anhydrous sodium chloride (99% metals basis, Sigma Aldrich), which acts as a pressure transmitting medium. These operations were carried out inside an argon-containing glovebox to prevent the hydration of powders. The die was held inside a custom-designed hot-press chamber, which utilizes a resistive heater enclosed in a flexible stainless steel bellows to allow hermetic sealing, transfer to a hydraulic press, and hot-pressing of the sample [20]. The samples were pressed at temperatures between 400 and 500°C and under a uniaxial load of 6350 kg-force (127 MPa). Pressure was increased manually, in a stepwise fashion, at a rate of 1000 kg-force every 10 minutes.

All ceramic samples were analyzed by x-ray diffraction using a PANalytical XPert3 MRD diffractometer equipped with a Cu/K α radiation source and a PIXcel detector array in a Bragg–Brentano geometry. Samples were loaded into an Anton-Parr DHS-1100 hot-stage and protected from the atmosphere by a graphite dome held under 3×10^{-1} mbar vacuum during the entire measurement. Scans were in the 2θ -range of 20 to 70°, with a step size of 0.0492° and an integration time of 150 s/step. Such a high integration time is necessary due to the high attenuation of x-rays by barium. Non-ambient temperature experiments were also performed on the hot-stage within the range of 25 to 350°C to observe the phase evolution of as-pressed samples. A slow heating rate of 10°C/min and a dwell of 10 min were programmed between each temperature step. Phase and Rietveld analyses were conducted using the HighScore Plus software version 4.1 from PANalytical.

For characterizations by transmission electron microscopy (TEM), 150 to 250 nm-thick samples were obtained by milling with a Zeiss 1540 focused ion beam (FIB) equipped with a scanning electron microscope (SEM). A 30-nm layer of Au/Pd was sputtered on the surface and welded to a probe to allow for sample lift off. The surface to

be examined was perpendicular to the polished surface of the ceramic. The sample was transferred immediately to the TEM sample holder, with a maximum of 5 min exposure to air for each sample. The resulting specimens were examined in an FEI Tecnai F30 TEM operated at 300 kV using both conventional bright-field imaging, and Selected Area Electron Diffraction (SAED).

Differential scanning calorimetry (DSC) measurements were carried out with a Netzsch model 204. Two successive scans from room temperature to 400°C were performed on a 1x2x2 mm chunk of ceramic held inside an aluminum crucible with lid. The scanning rates of 10°C/min and 20°C/min were used for the two runs respectively.

3. Results

3.1 Effect of pressing temperature on BaCl_2 ceramic samples

Figure 1 shows a side-by-side comparison of samples pressed between 400 and 500°C. On this picture, the BaCl_2 core of each sample is surrounded by the outer rim of pressure-transmitting NaCl. The most transparent BaCl_2 samples are produced at 450°C and the slight differences in temperature on either side of this temperature optimum drastically reduce the transparency.

Figure 1 Side-by-side comparison of 1 mm-thick BaCl_2 ceramic samples hot-pressed at five different temperatures. The BaCl_2 core of each sample is surrounded by an outer rim of NaCl.

3.2 X-ray diffraction on as-pressed samples

XRD patterns have been recorded for samples pressed at a range of temperature between 400 and 500°C (Figure 2). Samples pressed at 400°C mostly exhibit the peaks of o- BaCl_2 (cotunnite, Pnma, #62). The intense peaks centered at 28.5° and the plateau beginning at 45° 2θ in Fig. 2, originate from the graphite dome, used to protect the

sample from the ambient atmosphere. Traces of NaCl contamination (peak at $31.5^\circ 2\theta$) are visible in the samples pressed at 400 and 500°C. When the pressing temperature reaches 425°C, the peaks predominantly correspond to c-BaCl₂ (fluorite, Fm-3m, #225) with a small volume fraction of o-BaCl₂. Samples pressed at 450°C exhibit a similar phase composition to those pressed at 425°C. At 475°C, only a small fraction of c-BaCl₂ is present, and none is found at 500°C.

Figure 2 XRD patterns of ceramics pressed between 400 and 500°C under 6350 kg-force. Orthorhombic and cubic peak positions are displayed according to ICD references PDF 98-001-5705 and PDF 00-024-0095 respectively.

The lattice parameters of each phase were found to be within 0.16% of the literature data (Table 1). Contrary to our experiments, the cubic BaCl₂ sample referenced in [21] was prepared by rapid quenching from 925°C to room temperature (ICD database PDF 00-024-0095). To our knowledge, it is the first time that cubic BaCl₂ is produced by hot pressing at such a low temperature.

Table 1 Room temperature values of the lattice parameters of barium chloride orthorhombic and cubic phases as determined from x-ray diffraction and compared to literature data. The last row shows the ratios dilation between the parameters and volumes of the orthorhombic and cubic cells ($a_{\text{ortho}}/a_{\text{cubic}}$, $b_{\text{ortho}}/a_{\text{cubic}}$, $c_{\text{ortho}}/a_{\text{cubic}}$, $V_{\text{ortho}}/V_{\text{cubic}}$).

	a (Å)	b (Å)	c (Å)	V (Å ³)	
o-BaCl ₂	7.8776±0.0002	4.7360±0.0001	9.4357±0.0003	352.03	[This work]
(Pnma)	7.865	4.731	9.421	350.55	[21]
c-BaCl ₂	7.315±0.0002	-	-	391.42	[This work]
(Fm-3m)	7.311	-	-	390.78	[22]
Dilation ratio	1.077	0.647	1.290	0.900	

Quantitative phase analyses performed by Rietveld refinement were used to assess the phase composition of the samples pressed between 400 and 500°C, as well as the residual strain and crystallite size of the major phase (Table 2). Instrumental broadening was accounted for by calibrating against a coarse, strain-free, tungsten powder sample provided by PANalytical. One can notice from Fig. 2, that the c-BaCl₂ peaks are broader than those of o-BaCl₂, and that, for a given phase, the peak width decreases with increasing processing temperatures. At temperatures of 475°C and above, the peak width of o-BaCl₂ is outside the acceptable range for broadening analysis.

Table 2 Rietveld refinement parameters obtained on BaCl₂ ceramic samples pressed at varied temperatures. To columns labeled f_{cubic} and f_{ortho} correspond to the mass fraction of c-BaCl₂ and o-BaCl₂ phase respectively. G and ϵ correspond to grain size and micro-strain measured from peak broadening.

Temperature	f_{cubic}	G_{cubic}	ϵ_{cubic}	f_{ortho}	G_{ortho}	ϵ_{ortho}
(°C)	(wt %)	(nm)	(%)	(wt %)	(nm)	(%)
400	15	-	-	85	145±100	0.396±0.015
425	99	44±1	0.262±0.004	1	-	-
450	94	72±2	0.273±0.004	6	-	-
475	11	-	-	89	259±26	<0.1
500	0	-	-	100	> 500	<0.1

Broadening analysis identifies nano-sized and strained grains in the sample pressed at low temperature (400°C), suggesting large degree of fragmentation and residual strain from the pressing operation. When the temperature is raised and c-BaCl₂ becomes predominant, the grain size is even smaller, and the micro-strain is reduced. These observations are consistent with a recrystallization event characterized by limited growth and subsequent plastic deformation imparting

strain. Finally, the predominantly o-BaCl₂ samples pressed at 475 and 500°C have negligible strain and a grain size near or outside the limits of broadening analysis. These observations suggest that the higher ductility and grain growth of o-BaCl₂ particles at higher temperatures leads to less fragmentation, larger grains, and less buildup of strain.

3.3 Electron Microscopy

The same series of samples pressed between 400 and 500°C were also examined in the SEM. Samples exhibiting predominantly the cubic phase show small, rounded fracture domains on the order of 1 μm (Fig. 3a). These are significantly larger than the crystallite sizes calculated from XRD line broadening. In higher temperature orthorhombic samples (Fig. 3b) the observed fracture boundaries are much larger (22 μm), but there is no reliable XRD size analysis for comparison. Fracture boundaries are also much more angular in Fig. 3b.

Figure 3 SEM micrographs of the fracture surfaces of a BaCl₂ ceramic samples pressed at (a) 450°C (b) and 500°C.

The ceramic sample processed at 450°C, which exhibits the highest transparency and the highest fractions of cubic phase, was selected for TEM analysis. Fig. 4a shows a porous slice isolated from the bulk of the ceramic. The porosity is believed to arise from interaction with the beam during milling as well as hydration/dehydration of the sample surface. SAED confirms the presence of c-BaCl₂ and the absence of o-BaCl₂ in Fig. 4b. Individual grains are difficult to make out in the images due to their small size relative to the thickness of the sample. A few clear boundaries in the selected area image of Fig. 4b

show oblong crystallites with a longer axis on the order of 100 nm and a shorter axis on the order of 30 nm, values that are consistent with those of Table 2.

Figure 4 (a) SEM micrograph showing the fracture surface of a sample pressed at 475°C. (b) Bright-field TEM image with indexed SAED pattern in insert, corresponding to the BaCl_2 cubic phase.

In contrast, a second sample, also extracted from the bulk of the same 450°C ceramic, reveals the presence of untransformed o- BaCl_2 grains embedded into the polycrystalline matrix of c- BaCl_2 (Fig. 5). The diffraction pattern obtained by SAED has been indexed according to the 0 1 0 zone axis, with all d-spacings and interplanar angles agreeing well with those measured by XRD. However, due to the small grain size of the cubic phase, and the limitations of SAED, we were not able to confirm if an orientation relationship exists between the cubic and orthorhombic phases at the interface.

Figure 5 A second slice of the 450°C sample showing the interface between an orthorhombic BaCl_2 single-crystal (1) and a cubic (2) polycrystalline region, as revealed by SAED (left images).

3.3 Temperature stability of the cubic phase

As seen above, a large molar fraction of the cubic phase is quenchable down to ambient conditions at certain pressing temperatures. Once at room temperature, c- BaCl_2 ceramics have been shown to remain stable for at least 12 months. In fact, annealing experiments carried out by x-ray diffraction on a hot-stage indicate that c- BaCl_2 does not fully revert to the orthorhombic phase until temperatures of about 300°C (Fig. 6a). Phase quantification by Rietveld analysis reveals that only small amounts (<14%) of orthorhombic phase are present below 300°C and that phase reversion occurs very sharply thereafter (Fig. 6b).

Figure 6 (a) XRD patterns collected under vacuum and at increasing annealing temperatures on a single sample of BaCl_2 ceramic, initially pressed at 450°C. (b) Mass fraction of orthorhombic phase determined by Rietveld refinement. The dashed line is to guide the eye only.

The differential scanning calorimetry experiments carried out at temperatures up to 400°C (a temperature slightly higher than the temperature range covered by the XRD experiments shown in Fig. 6), show no specific thermal signature associated to the phase reversion detected by XRD near 250°C. This is true for both 10°C/min and 20°C/min heating rates and the 10°C/min curve is shown in Fig. 7.

Figure 7 DSC signal for a piece of c-BaCl_2 ceramic sample at a heating rate of 10°C/min.

4. Discussion

By hot pressing with an NaCl pressure transmitting medium, we have showed that BaCl₂ powders undergo an orthorhombic-to-cubic phase transition, which enables their densification and the production of transparent ceramics. We now discuss the conditions pertaining to this unusual approach.

4.1 Nature of the observed transition

Previous high-pressure studies, carried out in diamond anvil cells (DAC) at ambient temperature, have revealed that orthorhombic BaCl₂ converts, to so-called post-cotunnite polymorphs of higher coordination with monoclinic and hexagonal symmetries, at 7 and 21 GPa, respectively [15,16]. These values lie far outside the range of pressures attainable by our press, which we estimate to be well under 2 GPa, that is, if we account for a tenfold stress-intensification factor in the early stages of powder compaction [23,24]. Also, contrary to DAC, our experimental conditions can produce a larger amount of shear [25]. Moreover, the lack of thermal signature associated to the phase conversion (Fig. 7) is consistent with a shear-induced athermal martensitic transition [26]. The symmetry-reducing operation between the c-BaCl₂ aristotype (fluorite, Fm-3m), with Wyckoff positions *4a*, *8c* and *8c*, and the o-BaCl₂ hettotype (cotunnite, Pnma), with Wyckoff positions *4c*, *4c*₁ and *4c*₂, is characterized by the coordinate transformation matrix $T=[(0\ 0\ 1)(-1\ \frac{1}{2}\ 0)(1\ \frac{1}{2}\ 0)]$, with origin offset $P=[\frac{1}{2}\ \frac{1}{4}\ \frac{3}{4}]$, [27,28]. With these, one can derive the lattice parameter relationships between the cubic and orthorhombic cells as well as show that this transformation preserves the cell volumes:

$$\mathbf{a}_{ortho} = a_{cubic}[001]_{cubic} \quad (1)$$

$$\mathbf{b}_{ortho} = a_{cubic} \frac{\sqrt{2}}{2} \frac{[110]_{cubic}}{\sqrt{2}} \quad (2)$$

$$\mathbf{c}_{ortho} = a_{cubic} \sqrt{2} \frac{[1\bar{1}0]_{cubic}}{\sqrt{2}} \quad (3)$$

$$V_{ortho} = V_{cubic} \quad (4)$$

We find that the experimentally determined cell dilatation ratios ($a_{\text{ortho}}/a_{\text{cubic}}$, $b_{\text{ortho}}/a_{\text{cubic}}$, $c_{\text{ortho}}/a_{\text{cubic}}$), given in Table 1, slightly differ from theoretical values (1, 0.707, 1.41) and that the volumes of the orthorhombic and cubic cells are not conserved as a truly martensitic transformation would. In fact, using DFT calculations, S. Boulfelfel *et al.* predicted a transformation path in calcium fluoride (isomorph to c-BaCl₂), which includes a component of shearing in the cation sublattice as well as a component characterized by anion shuffles between sites[29], which support of these discrepancies. Our investigations by TEM were not able to resolve any topotactic relationship at the interface of the orthorhombic and cubic phases that would further validate this mechanism.

Assuming a mostly martensitic transformation, one can use a Clausius-Clapeyron relationship to estimate the magnitude of shear stress, $\tau = -\frac{\Delta s_{\alpha\beta}}{v_o} \frac{\Delta b}{b} \Delta T$, necessary to initiate the transformation on a single grain of o-BaCl₂, as proposed by A.G. McLellan [30]. With the experimental transformation strain $\Delta b/b=1-0.65$ (Table 1) and temperature shift $\Delta T=500^\circ\text{C}$, an entropy variation $\Delta s_{\alpha\beta}=14$ J/mol/K [24], and a molar volume $v_o=55 \times 10^{-6}$ m³/mol, one finds $\tau=45$ MPa. While it is well within the capability of the nominal uniaxial stress in our press, this number is difficult to relate to the actual resolved shear stress acting on a single pair of similarly oriented particles. Given the random orientation of the powder compact, the nominal uniaxial stress would in fact need to be much higher in order to initiate transformation in almost all grains. Because the Clausius-Clapeyron formulation does not adequately describe a powder compact under a complex state of stress, we propose the following method to describe the phase transition.

4.2 Stress-induced reverse martensitic phase transition

The elastic behavior and phase composition under stress in a polycrystalline material has been treated by micromechanical methods involving the homogenization of elastic properties, as well as a free-energy based phenomenological approach for application to dense shape-memory alloys[31,32]. In its simplest form and limiting this discussion to the first thermodynamic principle, i.e. neglecting energy dissipation rates during the powder compact deformation, the effect of combined isostatic and shear

stresses on the phase content can be approached as follow. The free-energy of the mixture of phase is written as[30,33,34]:

$$\mu = \lambda_{\alpha}\mu_{\alpha} + (1 - \lambda_{\alpha})\mu_{\beta} + E_{coh}(\lambda_{\alpha}) \quad (1)$$

where μ_{α} and μ_{β} are the chemical potentials of the cubic (α) and orthorhombic (β) phases, λ_{α} ($0 \leq \lambda_{\alpha} \leq 1$), the degree of advancement of the phase conversion and, $E_{coh}(\lambda_{\alpha})$, a coherence energy term. Under a state of stress characterized by the tensor σ_{mn} , the chemical potential of each phase i ($i=\alpha,\beta$) becomes:

$$\mu_i = \mu_i^o + S_{klmn}^i \sigma_{mn} \sigma_{kl} \quad (2)$$

where $\mu_{\alpha,\beta}^o$ is the chemical potential in the absence of any external stress and S_{klmn}^i the compliance tensor. At equilibrium, $\frac{\partial \mu}{\partial \lambda_{\alpha}} = 0$, and one finds:

$$\Delta \mu_{\alpha\beta}^o + \frac{\partial E_{coh}}{\partial \lambda_{\alpha}} = \frac{1}{2} (S_{klmn}^{\alpha} - S_{klmn}^{\beta}) \sigma_{mn} \sigma_{kl} \quad (3)$$

which becomes, after separating the isostatic (σ) and deviatoric (s_{mn}) components of the stress tensor ($\sigma_{mn} = \sigma \delta_{mn} + s_{mn}$):

$$\Delta \mu_{\alpha\beta}^o + \frac{\partial E_{coh}}{\partial \lambda_{\alpha}} = \frac{1}{2} \Delta S_{kkmm}^{\alpha\beta} \sigma^2 + \frac{1}{2} [\Delta S_{klmm}^{\alpha\beta} s_{kl} + \Delta S_{kkmn}^{\alpha\beta} s_{mn}] \sigma + \frac{1}{2} \Delta S_{klmn}^{\alpha\beta} s_{mn} s_{kl} \quad (4)$$

In their polycrystalline forms, the compliance tensors of the orthorhombic and cubic phases reduce to isotropic forms (e.g. Hill average), which allow further simplification:

$$\Delta g_{\alpha\beta} = \Delta \mu_{\alpha\beta}^o + \frac{\partial E_{coh}}{\partial \lambda_{\alpha}} = \frac{1}{2} \Delta K^{\alpha\beta} \sigma^2 + \frac{1}{2} \Delta S_{44}^{\alpha\beta} J_2 \quad (5)$$

In this expression, J_2 represents the second deviatoric stress invariant, whereas $\Delta K^{\alpha\beta} =$

$K^{\alpha,poly} - K^{\beta,poly}$ and $\Delta S_{44}^{\alpha\beta} = 1/G^{\alpha,poly} - 1/G^{\beta,poly}$ are the differences in isothermal compressibilities and shear modulus reciprocals between the polycrystalline forms of c- and o-BaCl₂ respectively. Hence, Eq. 5 takes a form akin to a von Mises condition for plastic yield:

$$1 = \left(\frac{\sigma}{\sqrt{\frac{2\Delta g_{\alpha\beta}}{\Delta K^{\alpha\beta}}}} \right)^2 + \left(\frac{\sqrt{J_2}}{\sqrt{\frac{2\Delta g_{\alpha\beta}}{\Delta S_{44}^{\alpha\beta}}}} \right)^2 \quad (6)$$

in which the elliptical branch, represented by Eq. 6 in the plane of stress invariants (σ , $\sqrt{J_2}$), defines the locus of the orthorhombic-to-cubic phase transition.

4.3 Phase-change sintering

The process of phase-change sintering results from the interplay between the yield of the powder compact (through the rearrangement of grains and the plastic deformation of individual particles above a given yield stress), a reverse martensitic transformation (enabling the formation of a crystalline phase of high-symmetry providing additional slip systems) and an associated flow rule under specific states of stress. The continuously changing characteristics of the microstructure (e.g. porosity, grain refinement) and their effects on the mechanical properties of the densifying ceramic complicate, at present, any attempt at a thorough quantitative analysis of the overall process. While values of the free-energies are referenced in the NIST-JANF database[35], only DFT-calculated values of the elastic constants have been determined by Kumar and Vadeshwar[36] and Curtarolo *et al.* [37]. In addition, most temperature dependencies of the terms entering Eq. 6 are unknown. However, to illustrate our concept of stress-induced phase-change sintering, we can schematically represent the loci for yield and phase change along with typical loading paths for a powder in closed die compaction (Fig. 8). The loading pathway accounts for the multiple stages of powder compaction, including particle flow, rearrangement and plastic yield. For samples pressed at 425°C and 450°C, the loading path must develop such that the phase change locus is exceeded (Fig. 8, trajectory ①). Provided the phase change is complete, the powder can now yield on any of the six

primary slip systems (001)[110] of the c-BaCl₂ fluorite structure in order to densify further. In the case of a lower pressing temperature, the phase change locus is broader and cannot be reached within the pressing die. Conversely, in the case of a higher pressing temperature, deviations in the yield and phase change loci are such that the loading path takes the sample above its yield strength, relaxing the state of stress to a value below the phase change locus.

Figure 8 Schematic conditions for ceramic phase-change sintering via stress-induced reverse-martensitic transformation. The x- and y-axes represent the isostatic and deviatoric stresses respectively. The grey lines depict the yield loci of powder compacts, with darker shades of pink corresponding to increasing powder compact densities. The green line defines the locus of phase transformation between the martensite (β -phase) and austenite (α -phase). Successful conversion to the α -phase is achieved when the strength of the β -phase powder compact allows for sufficient elastic energy storage (trajectory ①). Trajectory ② corresponds to a traditional compaction route without phase conversion.

Upon creation of finely grained c-BaCl₂ phase from nucleation and growth during the martensitic transformation combined with subsequent plastic deformation, a moderate cooling rate of 10°C/min is sufficient to quench the phase to room temperature and maintain that stability upon re-heating. Previous studies were successful in quenching coarse grained c-BaCl₂ when stabilized with up to 12.5% lanthanum or cerium[38]. In this study, the stability of the cubic phase arises from the nano-structuring of c-BaCl₂.

Hence, stress-induced polymorphic transformations complement the list of deformation processes, including grain rearrangement, grain boundary sliding and diffusion processes that are more traditionally used in ceramic processing. Not only the use of a high-pressure aristotype with cubic symmetry helps augmenting the plasticity of the phase and its densification, but it also eliminates birefringence-induced light scattering at crystallite interfaces, increasing the bulk optical transmission of densified ceramics.

5. Conclusion

We report experimental evidence of a stress-induced displacive polymorphic phase transformation for birefringent orthorhombic to optically isotropic cubic barium chloride at 450°C. This phase conversion allows the fabrication of fine-grained transparent ceramics of this material, a useful infrared and scintillation material, by simple powder compaction. While cubic BaCl₂ is a metastable phase at room temperature, it is retained in that structure at temperatures up to 300°C upon reheating and once the load is removed. At present, simultaneous phase transition and densification in this material are understood as a delicate interplay between the thermodynamic effect of the externally applied stress on the transition temperature, the loading path, and yield behavior of the powder compact. This mechanism may be applicable to similar materials, and additional characterizations will be needed to further our quantitative understanding of this process.

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